DIFFUSION IN LIQUIDS

A THESIS

Presented to

The Faculty of the Graduate Division

by

David Bowen, Jr.

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy in the School of Chemical Engineering

Georgia Institute of Technology

January, 1965

DIFFUSION IN LIQUIDS

Approved: [signature]

Chairman

Date approved by Chairman: June 15, 1965

DEDICATION

To my wife,

Luvoise,

whose love, patience, and understanding

have been sorely tried.

ACKNOWLEDGMENTS

The author is grateful to Dr. J. D. Fleming, Jr., who was his advisor for this study. His constructive criticisms and helpful suggestions facilitated the completion of the research work. The comments and advice offered by Dr. Henderson C. Ward and Dr. Charles W. Gorton, who served as members of the thesis committee are also appreciated. The author is also indebted to Dr. H. V. Grubb, Director of the School of Chemical Engineering, for his personal assistance and for the support which the School gave to this investigation.

Thanks are extended to the staff of the Rich Electronic Computer Center for their assistance in the examination of data and to the staff of the Price Gilbert Library for their excellent cooperation and assitance in locating references.

The author wishes to express his appreciation to Dr. J. A. Knight and Dr. R. F. Hochman for providing part-time employment during the completion of this investigation.

Early work in the degree program was made possible by the sponsorship of Kaiser Chemical Company during the academic years of 1961-1962 and 1962-1963. This assistance is gratefully acknowledged.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

NOMENCLATURE

A	Arnold association factor	
a	activity	
B	constant	
C	concentration	moles/cm^3
C_p	heat capacity at constant pressure	cal/mole $^{\circ}$ K.
D	diffusion coefficient	cm^2/sec
D^*	diffusion coefficient at infinite dilution	cm^2/sec
F	Wilke's solvent factor	T/μ D
G	Gibbs free energy	cal/mole
G^*	Gibbs free energy of activation	cal/mole
H	heat of vaporization	cal/mole
h	plank constant	6.62×10^{-27} erg sec
J	molar flux	moles/cm^2 sec
K	arbitrary constant	
k	Boltzman constant	1.38×10^{-16} erg/$^{\circ}$ K.
L	overall length	cm
M	molecular weight	g/mole
m	mass	g
N	Avogadro's number	6.024×10^{23} molecules/mole
N_A	mole fraction of component A	
N_B	mole fraction of component B	
P	pressure	gm/cm^2

NOMENCLATURE (Continued)

Q	flow rate		cm^3/sec
R	gas constant		cal/^{o} K. mole
R_t	remainder at time t		
r	radius		cm
S	sum of solute and solvent diameters		cm
s	estimated population variance		
T	temperature		^{o} K.
t	time	In Chapter II	sec
		otherwise	min
U	velocity		cm/sec
u	velocity of sound		cm/sec
V	molal volume of liquid		cm^3/mole
V_s	molal volume of solid		cm^3/mole
v	volume per molecule		cm^3
v_o	occupied volume per molecule		cm^3
X	length		cm
Z	axial distance		cm
Greek			
γ	activity coefficient		
Δ	increment symbol		
θ	radial angle		radians
λ	distance between equilibrium positions		cm
λ_1, λ_2,λ_3	distances between molecules in the forward, sidewards, and vertical directions		cm

NOMENCLATURE (Concluded)

μ	viscosity	poises
ξ	association factor	
π	constant = 3.1416	
ρ	density	g/cm^3
σ	number of nearest neighbors	
τ	nearest neighbors in one plane	
Φ	Stokes-Einstein friction factor	erg sec/cm^2
ψ	Wilke's association factor	

Subscripts Not Defined Above

B	value for the stirred bath
D	value for diffusion
F	value for the fritted disc
g	value for the gas phase
i	value for the i^{th} component
r	value for the radial direction
t	value at time = t
u	value for the solute
v	value for the solvent
Z	value for the axial direction
θ	value for the radial direction

SUMMARY

The development of more fundamental mass transfer correlations has been greatly accelerated by the increasing availability of rapid computation equipment. This has caused an increase in the need for basic experimental diffusion data, but such data are not generally available in the literature. In order to overcome this deficiency in experimental diffusion data, a number of estimation methods for the diffusion coefficient have been proposed by several investigators. While some of the proposed methods have been shown to be inadequate for engineering estimates, lack of experimental data has prevented evaluation and improvement of the other estimation methods.

The purpose of this investigation was to study the effect of temperatures ranging from 195° K. to 368° K. on the diffusion coefficient of 0.111 molar tritiated water in methanol, 2-propanone, and 2-butanone, and of 0.0991 molar tritiated methanol in 2-propanone, 2-butanone, 2-pentanone, 2 methyl,4-pentanone, and 2-heptanone. The data over this wide temperature range were employed to select a temperature function for the diffusion coefficient and to develop an improved estimation method.

The decision to study the effect of temperature on diffusion was based on the observation that no system included in the extensive compilations of diffusion data by Johnson and Babb, Wilke, and Wilke and Chang had a temperature range greater than 70° K. Since most of the data recorded fell in the temperature interval of from

268° to 360° K., this represents a change of only approximately 25 percent in absolute temperature. The temperature interval investigated in this research was from 195° to 368° K. which represents an 89 percent change in absolute temperature.

The method used in the measurement of the diffusion rate was a modification of the porous frit system used previously by Wall, Grieger and Childers and by Nelson and Kraus. In this system, tracer labeled solute was allowed to diffuse from the capillaries of a calibrated fritted disc into a stirred bath. Measurement of the changing bath tracer concentration as a function of time permitted the calculation of the diffusion coefficient. The self-diffusion coefficient of water was used to calibrate the frits used in this study.

The viscosity of the solution appears as a parameter in most of the diffusion coefficient estimation methods. This indicated the necessity for measuring the viscosity of the eight solutions as a function of temperature. Cannon-Fenske calibrated viscometers were used to determine the kinematic viscosity of these solutions at each temperature where the diffusion rate was to be studied.

The density of the various solutions as a function of temperature was measured by means of a Westphal balance.

The absolute viscosity in centipoises was determined by using the experimental density and kinematic viscosity data. Polynomial equations for the density and absolute viscosity for each of the systems studied were derived from the experimental data. Tables of viscosity and density versus temperature were also computed from these equations.

The values for the diffusion coefficient were determined for each

of the eight systems over as wide a temperature range as was possible without having freezing or vaporization problems. This wide temperature interval gave an associated minimum change in the measured diffusion coefficient and viscosity of at least a factor of five and eight respectively.

The data for all eight systems fitted the relation

$$D = K_{system} (T/\mu_v)^{1.0} \qquad (1)$$

with a maximum deviation of ± 14 percent from the average value of K for any system. Since the value of (T/μ_v) varied by a factor of 10 to 45 over this temperature interval, the relative magnitude of the error in K was seen to be small.

Several diffusion coefficient estimation methods with the function $(T/\mu_v)^{1.0}$ were compared with the experimental data. All of the estimation methods predicted values for D which were too large for the diffusion of water. It was thought that this discrepancy might be attributed to the fact that the solvents had polar groupings which might have formed hydrogen bonds with the water molecules, thus reducing the diffusion rate. The estimated values for the diffusion rate of methanol in the ketone series were all high for diffusion in acetone, but tended to decrease toward the experimental values as the solvent chain length increased. Several of the methods gave predicted values lower than the experimental values for diffusion in Methyl n-Amyl Ketone.

By examining a large collection of data, it was concluded that

for self-diffusion

$$\frac{D\mu}{T} \times 10^{10} = 4.0 \tag{2}$$

The constant value of $D\mu/T$ for self-diffusion seems to refute the theoretically derived relation

$$\frac{D\mu}{T} = K \left(\frac{N}{V}\right)^{1/3} \tag{3}$$

For dilute binary diffusion, the data were correlated by the relation

$$\frac{D\mu_v}{T} = K_D \left(\frac{V_v}{V_u}\right)^{0.55} \tag{4}$$

where the value of K_D is a property of the solvent. For systems where the value of K_D cannot be determined from experimental data, the relation

$$\frac{D\mu_v}{T} \times 10^{10} = \left[0.350 \left(\frac{H_v}{M_v}\right)^{0.50}\right] \left(\frac{V_v}{V_u}\right)^{0.55} \tag{5}$$

may be used with the limiting conditions that:

1. The minimum value for the bracketed expression is 3.3.
2. The maximum value for the volume ratio, (V_v/V_u), is 2.5.

Equation 5 was shown to predict successfully the value of $\frac{D \mu_v}{T}$ for a number of systems including water, methanol, benzene and carbon tetrachloride as solvents.

The most important conclusion drawn from this work is that the relation

$$\frac{D \mu}{T} = K \tag{6}$$

was found to characterize every self-diffusion and binary diffusion system studied.

CHAPTER I

INTRODUCTION

Definition of the Problem

The Fick equation for diffusion is given by

$$J_A = -D \frac{dC_A}{dX} \tag{1.1}$$

where the constant of proportionality, D, is the diffusion coefficient. This coefficient is one of the fundamental variables in liquid mass transfer operations. For reactions occurring in the liquid phase, D is one of the primary rate controlling factors. The design of bubble cap trays for distillation columns, the calculation of theoretical unit height for packed column absorbers and the design of solvent extraction systems are typical of other processes in which D is important. The development of more fundamental mass transfer correlations and of more rapid computation methods has increased the need for diffusion data, but such data are generally not available in the literature.

Efforts to evaluate the effect of temperature on the diffusion coefficient have been frustrated by the lack of experimental diffusion data. The maximum temperature range covered in the literature for systems other than liquid metals is only 70° K. (1). An extensive compilation of experimental data by Johnson and Babb (2) for diffusion in non-

electrolytes shows that most of the available data fall in the temperature interval of 273° to 333° K.

In order to overcome this deficiency in basic data, several methods for estimating D have been proposed and used with varying degrees of success. These methods may be broken into two rough categories based on whether the method was based on a theoretical rather than on an empirical viewpoint. The theoretical methods have not generally been as successful as the empirical methods in predicting values of the diffusion coefficient, and this is due to the lack of a completely acceptable theory and model for the liquid state.

The object of this research was to study the effect of temperature on the diffusion rate of tritiated water (H_2O) in methanol (MeOH), acetone (ATN), and 2-butanone (MEK) and on the self-diffusion rate of tritiated methanol in acetone, 2-butanone, 2-pentanone (MPK), 2-methyl, 4-pentanone (MiBK), and 2-heptanone (MAK). The concentration of the water solutions was 0.111 molar and the concentration of the methanol solutions was 0.0991 molar in all of the systems utilized. Table 1 shows the temperatures at which diffusion measurements on each of the systems were made.

The method used in the measurement of the diffusion rate was a modification of that system used in the measurement of the diffusion rate by Wall, Grieger and Childers (3) and by Nelson and Kraus (4). In this system, tracer labeled solute was allowed to diffuse from the capillaries of a fritted disc into a stirred bath. Measurement of the changing bath tracer concentration as a function of time permitted the calculation of the diffusion coefficient as described in Chapter II.

Table 1. Temperatures at Which the Diffusion Coefficients of the Various Systems Were Measured

T^{o} K.	solv.-solu. ATN - H_2O	solv.-solu. MEK - H_2O	solv.-solu. MEOH - H_2O	solv.-solu. ATN - MEOH
195	X	X	X	X
233	X	X	X	X
253	X	X	X	X
273	X	X	X	X
293	X	X	X	X
323	X	X	X	X

	MEK - MEOH	MPK - MEOH	MiBK - MEOH	MAK - MEOH
195	X	X	X	
233	X	X	X	
253	X	X	X	X
273	X	X	X	X
293	X	X	X	X
323	X	X	X	X
353		X	X	
368			X	X

Data obtained from the wide temperature range considered here were used to determine a temperature function for the diffusion coefficient. This experimentally derived temperature function for the diffusion rate was compared with that predicted from theoretical considerations and with that obtained from consideration of data available in the literature. An attempt to present an improved estimation method utilizing these results was made.

Review of Estimation Methods for the Diffusion Coefficient

Stokes-Einstein Equation

The classical diffusion equation was derived by considering that the motion of molecules or "particles" of the diffusing species was able to be described as a "random walk process." Figure 1 shows such a system with a concentration gradient $\Delta C/X$ around the central zero plane. The symbol, X, has been chosen as the average displacement of the particles for each step in the random walk. For a sufficiently large number of particles, and considering only motion perpendicular to the zero plane, it can be seen that there is a net flow of particles in the direction of decreasing concentration described by

$$J = -X\left(\frac{\Delta C}{2}\right) \tag{1.2}$$

When this result is compared with the permeation obtained from the Fick equation, we obtain

$$Dt\left(\frac{\Delta C}{X}\right) = J = X\left(\frac{\Delta C}{2}\right) \tag{1.3}$$

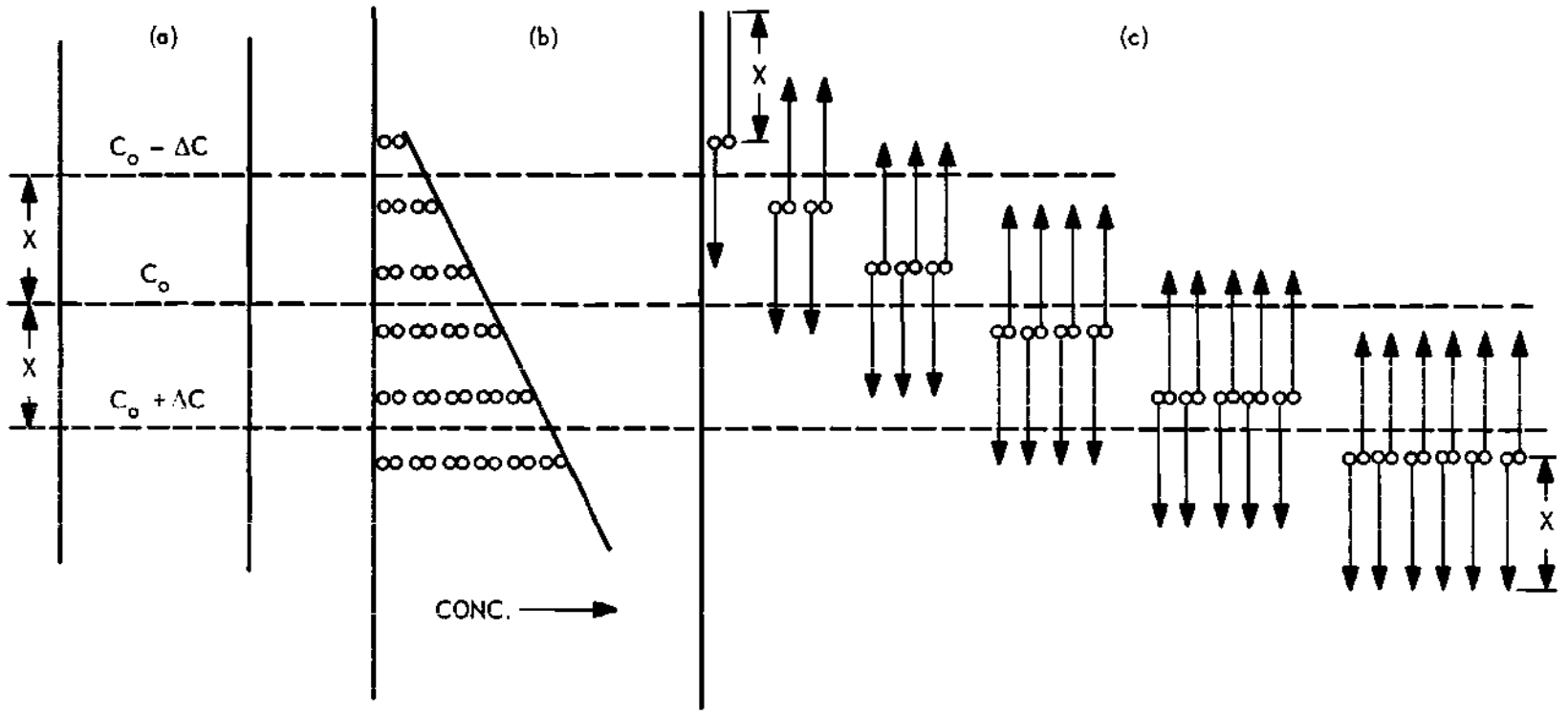

Figure 1. Net Permeation Due to Concentration Difference in a Random Walk Process.

Combining the two results and rearranging gives

$$D = X^2/2t \tag{1.4}$$

which is Einstein's law (5). This very simple law is of great importance in diffusion systems, since it shows that the average displacement in a random walk is a function of the square root of time. It also shows that Fick's law, which was based on macroscopic measurements, is the net result of random motion of individual particles.

By considering that the thermal agitation energy, or the displacement energy, of each particle was proportional to kT, Einstein was able to obtain an equation containing the frictional resistance encountered by the diffusing species under terminal velocity conditions. The result (3),

$$D = kT/\Phi \tag{1.5}$$

is Einstein's law of diffusion. Its importance lies in the linking of the diffusion coefficient to the thermal energy and to the frictional characteristics of the particle. It is noted that the mass of the particle is not a factor in the equation since all particles are assumed to have the same thermal energy.

By assuming that the liquid was a continuum, that the particles were spherical, and that the terminal Reynolds number was low, Stokes (6) was able to solve equation 1.5 for the friction factor Φ.

The result,

$$\Phi = 6 \pi \mu r \tag{1.6}$$

when combined with the Einstein equation for diffusion, is the Stokes-Einstein equation,

$$D = kT/6 \pi \mu r \tag{1.7}$$

This equation has been very successful in predicting diffusion in liquids for particles which range in size from 10 to 10^5 A^o in radius. For particles larger than 10^5 A^o, the velocity reached is too high for the assumption of low Reynolds number to hold. For particle sizes less than 10 A^o, the liquid no longer appears as a continuum. The chief contribution of this equation to normal molecular diffusion is in the indication that the temperature function for diffusion may be either $T^{1.0}$ or the group $(T/\mu)^{1.0}$. Several correlations show the general relationship

$$D = K_{system} (T/\mu)^{1.0} \tag{1.8}$$

Theory of Reaction Rates

Eyring et al. (7) developed a method for calculating D based on the theory of absolute reaction rates. The starting point in his development was the equation

$$R = (kT/h) C_o e^{-\Delta G^*/RT} \tag{1.9}$$

Equation 1.9 is completely general, stating that the rate of reaction is determined by the product of the number of activated complexes and the frequency group (k T/h).

By considering flow as a rate process aided by external forces, the following equation for viscosity was next developed:

$$\frac{1}{\mu} = \frac{\lambda^2 \lambda_2 \lambda_3}{\lambda_1 h} e^{-\Delta G^*/RT} \qquad (1.10)$$

The model for diffusion was considered to be the same as that for viscous flow since both processes were thought to consist of activated molecules moving from one lattice position to another. The relationship for D therefore became

$$D = \frac{\lambda^2 kT}{h} e^{-\Delta G_D^*/RT} \qquad (1.11)$$

The energy of activation for the process of diffusion and viscous flow was considered equal so that combination of equations 1.11 and 1.10 gave

$$D = \frac{\lambda_1 k}{\lambda_2 \lambda_3} \left(\frac{T}{\mu}\right)^{1.0} \qquad (1.12)$$

which has the same temperature viscosity grouping as the Stokes-Einstein Equation, Equation 1.7. Equation 1.12 has been shown (8) to give results of the proper order of magnitude, but with variations of a factor of three to five between experimental and calculated values.

Eyring's Significant Structure Theory for Liquids

Eyring et al. (9, 10) proposed a second method for calculating D based on the Significant Structure Theory of Liquids. This method was based on a model of the liquid state which consisted of an equilibrium concentration of rapidly moving gas-like vacancies along with a very short range ordered solid-like phase. The properties of the liquid were developed by partitioning the contributions of the two phases to the property in question.

The self-diffusion coefficient is given by the relationship

$$D = \frac{kT}{\lambda\,(V_s/N)^{1/3}\mu}\;\frac{d\ \mathrm{Ln}\ a_i}{d\ \mathrm{Ln}\ C_i} \tag{1.13}$$

where

$$\mu = \frac{V_s}{V}\,\mu_s + \frac{V - V_s}{V}\,\mu_g \tag{1.14}$$

For several systems in which there is sufficient data, diffusivities have been predicted successfully by equation 1.13, but for most engineering applications, lack of data precludes the use of this equation.

Arnold's Kinetic Theory

Arnold (11) was the first to develop a successful kinetic theory for diffusion in liquids. As a starting point, the following assumptions were made:

1. Only binary collisions can occur.
2. Intermolecular forces and attractions are negligible.

3. The volume of the molecules does not affect the collision rate. The following equation resulted:

$$D = \frac{B\sqrt{(1/M_u) + (1/M_v)}}{S^2} (V_v) \qquad (1.15$$

where M_u and M_v are the molecular weights of the solute and solvent, S is the sum of the molecular diameters, V_v is the molar volume of the solvent and B is a constant of proportionality.

It was recognized that the assumptions listed above were more representative of the gaseous state than of the liquid state, and correction factors were therefore introduced into the denominator. The introduction of factors A_u for solute association, A_v for solvent association and the square root of the viscosity for intermolecular forces caused the final form of the equation to be

$$D = \frac{B\sqrt{(1/M_v) + (1/M_u)}}{A_u S^2 A_v \mu_v^{1/2}} \qquad (1.16)$$

The results of calculations performed by Caldwell and Babb (12) with the Arnold equation show that for dilute ideal systems, the average deviation from measured values is approximately ten percent.

The S^2 term in the denominator of this equation is proportional to the molecular volume raised to the two-thirds power rather than the one-third power proposed by the three previous methods.

If the necessary data for the association parameters are available,

the Arnold equation may be used with considerable success for dilute solutions.

Method of Kamal and Canjar

By assuming that the form of the Einstein equation is correct, Kamal and Canjar (13) derived an equation for the binary diffusion coefficient at infinite dilution based on a statistical mechanics approach. The final result takes the form

$$D^{*} = B\, f(\Delta H) \tag{1.17}$$

where

$$B = \left[1.2021 \times 10^{-8}(RT/\pi M)^{1/2}\, V_o^{1/3} A\right]_{\text{solvent}} \tag{1.18}$$

$$A = \left\{\left[1.6(v_o/v) + 2.56(v_o/v)^2\, N\, g^{(2)}(\sigma)\right](v_o/v)^{-2/3}\right\}_{\text{solvent}} \tag{1.19}$$

$$f(\Delta H) = \left[RT/(24\Delta H_{vap} - 39RT)\right]_{\text{solute}} \tag{1.20}$$

$$g^2(\sigma) = \left[1 + 2.5(v_o/v) + 4.5864(v_o/v)^2\right]_{\text{solvent}} \tag{1.21}$$

and the value (v_o/v) can be determined from the velocity of sound in the liquid by the relation

$$u = \left\{ \left[\frac{1 - 2/3(v_o/v)^{1/3}}{1 - (v_o/v)^{1/3}} \right] \left[\frac{C_p RT/M}{C_p(1 - 2/3(v_o/v)^{/}) - R} \right]^{1/2} \right\}_{\text{solvent}} \qquad (1.22)$$

The major assumptions used in the derivation are:

1. The molecules are rigid spheres.

2. The heat of vaporization of the solute is the primary factor in its contribution to the diffusion rate.

For use under conditions other than infinite dilution, the diffusion coefficient, D^*, is calculated for both the solute and solvent and the relationship

$$D = (N_A D^*_B + N_B D^*_A)\left[1 + N_B \left(\frac{\partial \text{ Ln } \gamma_B}{\partial N_B}\right)\right] \qquad (1.23)$$

is employed to obtain D. This approach is moderately successful in predicting diffusivities, but the data required for its use are not generally available.

Method of Li and Chang

Starting with the Stokes-Einstein equation, Li and Chang (14) proposed an equation of the form

$$\frac{D\mu}{kT} = \frac{1}{2\pi}\left(\frac{N}{V}\right)^{1/3} \qquad (1.24)$$

for self-diffusion in liquids. Li and Chang also noted that, if in the Eyring Equation, Equation 1.12, the λ's are assumed proportional to the

intermolecular distance, the equation may be rearranged to show that

$$\frac{D\mu}{kT} = \left(\frac{N}{V}\right)^{1/3} \tag{1.25}$$

This equation differs from equation 1.24 only by the absence of the factor 2π. This difference was assumed to occur in Eyring's derivation of the viscosity relation due to his not considering the relative velocity between molecules as well as the average velocity. By considering the relative motions of all the closest neighbors of a molecule, the diffusion equation assumes the form

$$\frac{D\mu}{kT} = \frac{\sigma - \tau}{2\sigma} \left(\frac{N}{V}\right)^{1/3} \tag{1.26}$$

For a cubic structure, the number of nearest neighbors is 6 and the number in one plane is 4. This gives

$$\frac{D\mu}{kT} = \frac{1}{6} \left(\frac{N}{V}\right)^{1/3} \tag{1.27}$$

which is very close to equation 1.24 in value. For several systems the agreement with experimental data is very good. Exceptions to the rule are methanol, ethanol and lead. If the fact that lead diffuses as an ion is considered, with the ion volume being about 30 percent that of the metal, this discrepancy disappears.

Method of Wilke

Wilke (1) proposed that the diffusion coefficient in dilute binary solutions of non-electrolytes could be related to the absolute temperature and the viscosity of the solvent by the relation

$$D = \frac{T}{\mu F} \tag{1.28}$$

where F was called the solvent factor. The fact that F remained essentially constant for four solvent-solute systems over a maximum temperature range of 70° C. was used to show that F was not significantly affected by changes in temperature. By plotting the solute molal volume as determined by the method of LeBas (15) versus F for 168 different systems, Wilke obtained a graphical correlation for F based on the solute molal volume and the association parameter of the solvent. The association parameter varies from 0.70 for benzene to 1.0 for water. Equation 1.28 yielded very good results, giving an average deviation of only 11 percent from experimentally derived values for the wide range of system types covered.

Method of Wilke and Chang

In the light of a large amount of new diffusion data, Wilke and Chang (16) were able to give a more detailed analysis of the contribution of the solvent and solute to the diffusion factor. The resulting equation

$$D = 7.4 \times 10^{-10} (\psi M_v)^{0.5} T/\mu_v V_u^{0.6} \tag{1.29}$$

distinguished between associated and unassociated solvents by the factor

Ψ and defined the exponent of the solute molal volume. It is to be noted that, although previous theoretical considerations had set the exponent of V as equal to 0.33, the experimental data reported in this work were better correlated by the use of 0.60 as the exponent.

The solvent association factor was reported as 2.6 for water, 1.9 for methanol, 1.5 for ethanol and 1.0 for unassociated solvents. This equation has been one of the more successful correlations, giving diffusion coefficients with an average deviation of only 12 percent from experimentally derived values for a wide variety of solute-solvent systems.

Method of Othmer and Thakar

By considering that the exponential form of Eyring's equation for diffusion,

$$D = K \exp (\Delta G^*_D/RT) \tag{1.30}$$

was correct in form, Othmer and Thakar (17) developed a reference substance method for estimating D. When equation 1.30 was differentiated with respect to T, the result had the same form as the Clausius-Clapeyron equation

$$d \text{ Ln } D = (\Delta G^*_D/RT^2)dT \tag{1.31}$$

$$d \text{ Ln } P = (H/RT^2)dT \tag{1.32}$$

When equation 1.31 was divided by equation 1.32, the following result was

obtained

$$\frac{d\ Ln\ D}{d\ Ln\ P} = \frac{\Delta G^*_D}{H} \tag{1.33}$$

The right hand side of equation 1.33 was assumed to be constant, and the following equation for D was obtained:

$$Ln\ D = \frac{\Delta G^*_D}{H} Ln\ P + K \tag{1.34}$$

A plot of the experimental data for water showed a discontinuity at 303° K. when equation 1.34 was used, so the solvent viscosity was used as a correlating factor with

$$Ln\ D = \left(\frac{\Delta G^*_D}{\Delta G^*_\mu}\right) Ln\ \mu + K \tag{1.35}$$

This choice was very successful, as it yielded lines with slopes of -1.07 to -1.15 for several solutes diffusing in water.

Fitting the data available for water and taking the average slopes gave

$$D \times 10^7 = 8.85/100\mu_w^{1.1}\ V_u^{0.6} \tag{1.36}$$

For solvents other than water, the following equation was proposed:

$$D \times 10^7 = 14 / \left[100\mu_w \right]^{(1.1 \frac{H_v}{H_w})} V_u^{0.6} \, 100\mu_v \text{ at } 20^\circ \text{ C} \qquad (1.37)$$

The exponent of the solute molal volume is seen to be 0.60, the same as in equation 1.29.

Equation 1.37 is not as successful in predicting values for the diffusion coefficient as is Equation 1.29.

Method of Scheibel

Scheibel (18) correlated the early graphical diffusion coefficient estimation method of Wilke by the empirical equation

$$F = 1.22 \times 10^7 \, V_u^{1/3} / \left[1 + \left(\frac{3V_v}{V_u} \right)^{2/3} \right] \qquad (1.38)$$

which results in

$$D = 8.2 \times 10^{-10} \frac{T}{\mu_v} \left[\left(1 + \left(\frac{3V_v}{V_u} \right)^{2/3} \right) / V_u^{1/3} \right] \qquad (1.39)$$

when equation 1.38 is combined with equation 1.28. The following conditions guide the general use of equation 1.39:

1. For water, if V_u is less than V_v, the ratio (V_v/V_u) is taken as equal to 1.00.

2. For methanol, if V_u is less than 1.5 V_v, the ratio (V_v/V_u) is set at 0.666.

3. For benzene, the maximum ratio of (V_v/V_u) is set at 0.500.

4. For other systems, the maximum ratio of (V_v/V_u) is set at 0.400. The use of equation 1.39 has been very successful, rivaling the correlation of Wilke and Chang in the low average percent deviation of estimated values of D from values derived from experimental data.

Method of Houghton

Starting with a cubic lattice structure and the Navier-Stokes equation, Houghton (19) developed the following relation for the self-diffusion coefficient in liquids:

$$D = RT\ \lambda^2\rho/24\ M\ \perp \qquad (1.40)$$

Since the experimental data were best fitted by the relation, $\lambda = 2v^{1/3}$, Equation 1.40 was rewritten

$$D = RT\ \rho\ v^{2/3}/6M\ \mu \qquad (1.41)$$

For 25 systems, the calculated values agreed with the measured values with an average deviation of nine percent.

This research will endeavor to determine the temperature function for self-diffusion and dilute binary diffusion in liquids by using a much wider temperature range than that found in any reported system. Verification of an estimation method for the diffusion coefficient described above or development of an improved estimation method by use of the experimental data will be attempted.

CHAPTER II

MATHEMATICAL DEVELOPMENT

The system studied consisted of a uniform, cylindrical, sintered glass frit saturated with a solution containing tracer labeled solute. This frit was suddenly immersed in a stirred bath of the same concentration as the solution contained within the frit, but with no tracer present. The volume of the bath was large compared with the pore volume of the frit and the bath was well stirred. As a result, the concentration of labeled solute in the bath was small compared with the initial concentration in the frit and was uniform throughout the bath. The concentration of labeled solute in the bath was thus small enough not to affect rate of diffusion, but still large enough to be measured with accuracy. The increasing tracer concentration in the bath could be used to determine the rate of loss of labeled solute from the frit. The following development describes the method used to calculate the diffusion coefficient of the labeled solute from measurement of the bath activity as a function of time.

The equation of continuity for the tracer in the frit with D and ρ assumed constant is:

$$\frac{\partial C_F}{\partial t} + \left(U_r \frac{\partial C_F}{\partial r} + U_\theta \frac{1}{r} \frac{\partial C_F}{\partial \theta} + U_Z \frac{\partial C_F}{\partial Z}\right) =$$

$$D\left(\frac{1}{r}\frac{\partial C_F}{\partial r} + \frac{\partial^2 C_F}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2 C_F}{\partial \theta^2} + \frac{\partial^2 C_F}{\partial Z^2}\right) \qquad (2.1)$$

No pressure gradient existed to cause bulk flow in the system and the frit was prepared to have a uniform initial concentration of tracer present. The fluid velocity in the frit was uniformly zero. Since the frit was sealed around its circumference by the frit holding assembly, no radial diffusion could occur to produce an angular concentration gradient. Wall et al. (3) have shown that radial diffusion is unimportant in thin fritted discs. As a result:

$$U_r = U_\theta = U_Z = 0 \qquad (2.2)$$

$$\frac{\partial C_F}{\partial r} = \frac{\partial^2 C_F}{\partial r^2} = \frac{\partial^2 C_F}{\partial Z^2} = 0 \qquad (2.3)$$

and equation 2.1 becomes

$$\frac{\partial C_F}{\partial t} = D\frac{\partial^2 C_F}{\partial Z^2} \qquad (2.4)$$

By assuming that the concentration of labeled solute outside the frit is held at zero, several solutions to equation 2.4 can be found. The solutions presented in equations 2.5 and 2.6 were taken from Carslaw and Jaeger (20).

$$C_F = \frac{4C_{FO}}{\pi} \sum_{n=o}^{\infty} \frac{(-1)^n}{(2n+1)^2} e^{-D(2n+1)^2 \frac{\pi^2 t}{L^2}} \cos (2n+1)\frac{\pi Z}{2L} \qquad (2.5)$$

and the average concentration is given by:

$$C_{F\ avg} = \frac{8C_{FO}}{\pi^2} \sum_{n=o}^{\infty} \frac{1}{(2n+1)^2} e^{-D(2n+1)^2 \frac{\pi^2 t}{4L}} \qquad (2.6)$$

The amount of tracer appearing in the stirred bath is:

$$V_B\ C_{Bt} = V_F\ (C_{FO} - C_{F\ avg\ t}) \qquad (2.7)$$

which can be rearranged to give:

$$C_{FO} - \frac{V_B}{V_F} C_{Bt} = C_{F\ avg\ t} \qquad (2.8)$$

But it is easily seen that:

$$C_{FO} = \frac{V_B}{V_F} C_{B\infty} \qquad (2.9)$$

where $C_{B\infty}$ can be measured for each experimental run. Substitution of equation 2.9 into equation 2.8 and rearranging gives:

$$\left(1 - \frac{C_{Bt}}{C_{B\infty}}\right) = \left(\frac{V_F}{V_B\, C_{B\infty}}\right) C_{F \text{ avg } t} \qquad (2.10)$$

By dropping the constant terms on the right hand side of equation 2.6 and substituting the remainder for $C_{F \text{ avg } t}$ in equation 2.10, we have

$$\left(1 - \frac{C_{Bt}}{C_{B\infty}}\right) = \left(\frac{V_F}{V_B\, C_{B\infty}}\right) \sum_{n=o}^{\infty} \frac{1}{(2n+1)^2}\, e^{-D(2n+1)^2 \frac{\pi^2 t}{4L^2}} \qquad (2.11)$$

Equation 2.11 converges rapidly and its value can be very closely represented by the term for n = o except for very short times. If the n = o term only is used, equation 2.11 becomes

$$\left(1 - \frac{C_{Bt}}{C_{B\infty}}\right) = Ke^{-D\, K_F\, t} \qquad (2.12)$$

This shows that if the log of $\left(1 - \frac{C_{Bt}}{C_{B\infty}}\right)$ is plotted versus t, a straight line of slope equal to $(-D\, K_F)$ should result. If the frit constant (K_F) is evaluated by use of a system with known D, then D for other systems can be determined from the slope of the line obtained by plotting the experimental data as outlined above.

CHAPTER III

EXPERIMENTAL EQUIPMENT

The Constant Temperature Bath

In order to carry out the proposed investigation on the effects of temperature on diffusion rate, a constant temperature bath was required which could furnish temperature control from 195° to 370° K. The bath designed to meet the requirement is shown in Figures 2 and 3. This bath permitted temperature control within ± 0.5° K. over the required temperature range.

Diffusion Chamber

The inner cylindrical container held the stirred bath, the sintered glass frit and the frit holder, and a Teflon coated magnetic stirrer. The ground glass flanged top was fitted with two ground glass sampling ports. A closed container was necessary to prevent loss of tracer containing material by evaporation and to maintain a controlled vapor space over the stirred bath.

One of the primary assumptions in the development of the mathematical model for the system was that the stirred bath had a uniform composition. This was also required if samples taken from the bath were to be independent of position. The Teflon coated magnetic stirrer produced the required turbulence to insure uniformity of the bath. Use of the stirrer also provided a slight improvement in temperature control.

The outer container held the temperature control bath, a magnetic

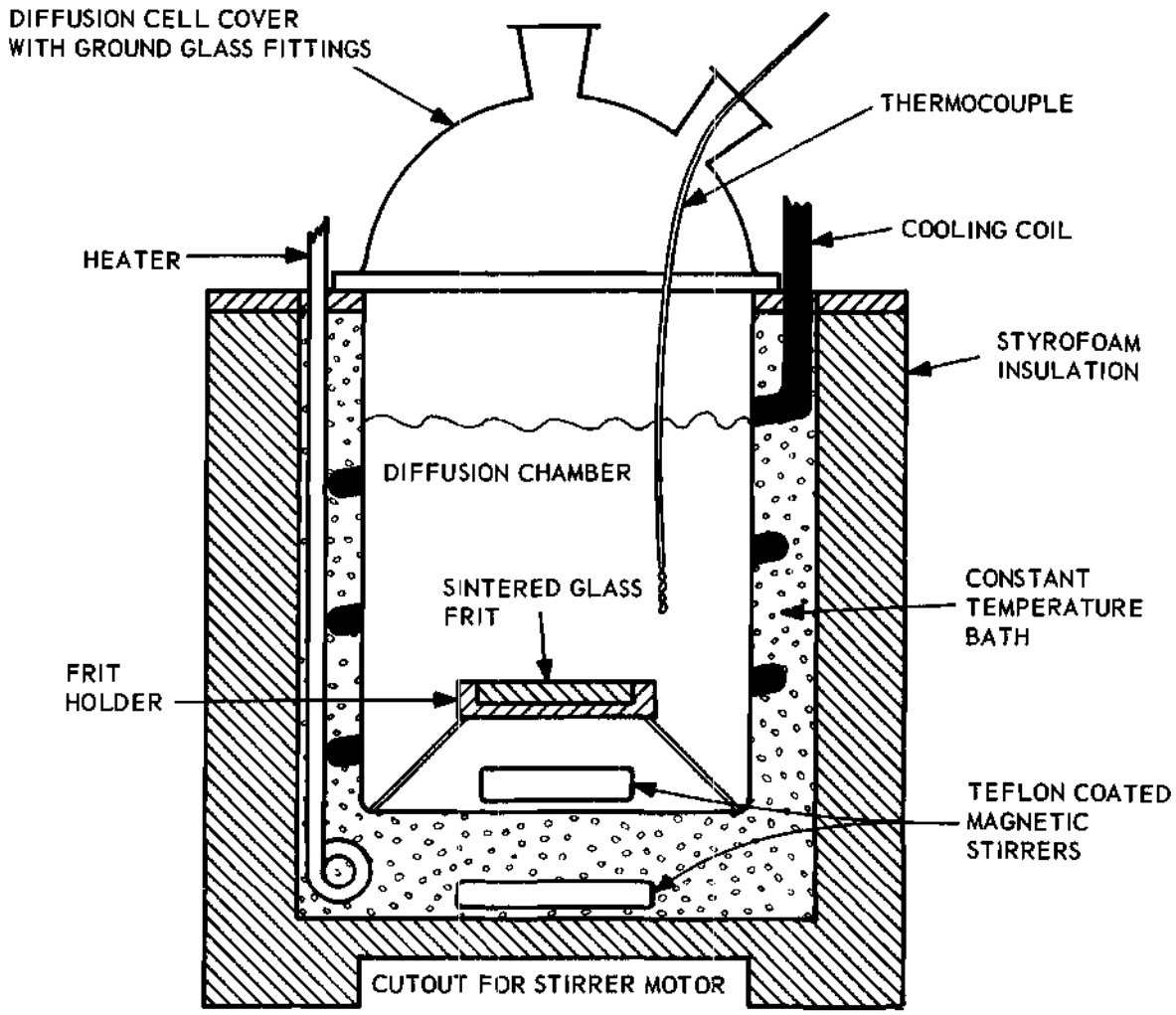

Figure 2. Detail of Diffusion Chamber of Constant Temperature Bath.

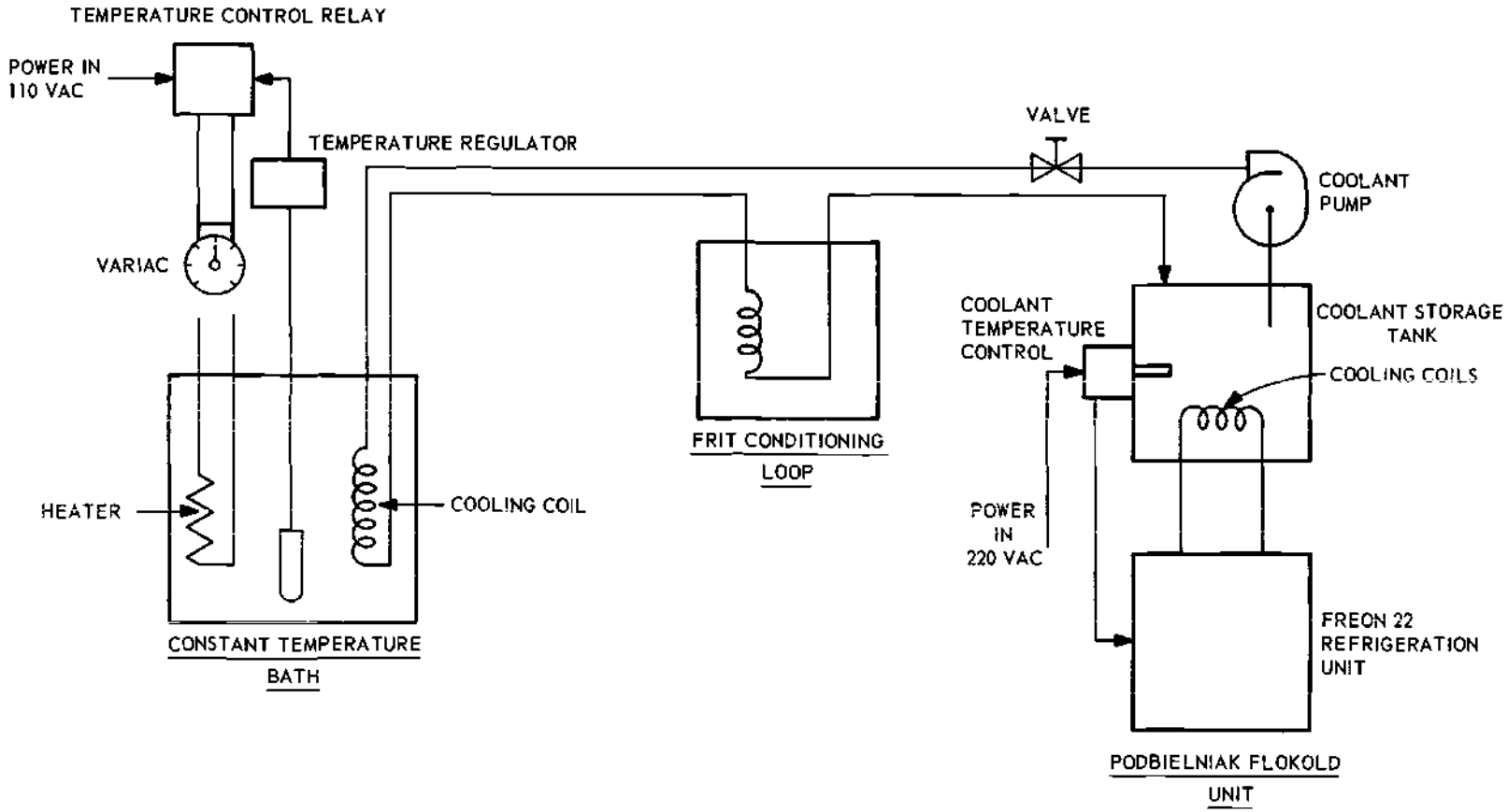

Figure 3. Schematic of Constant Temperature Bath.

stirrer, a thermo-regulator, a heat source, and a heat sink. The control bath was either methanol, water, or cooking oil according to the temperature of the experimental run being conducted.

The heat source was a small 300 watt immersion heater. The power input to this heater was controlled by use of a Variac voltage transformer.

The heat sink consisted of three turns (five feet) of one-quarter inch copper tubing immersed in the control bath. The flow of coolant through the heat sink was controlled by a valve.

Two different thermo-regulators were used in order to cover the temperature range studied. A Precision Scientific Company adjustable mercury thermo-regulator was used for temperatures from 273° to 370° K. For the low temperature experimental runs, a gas actuated thermo-regulator was fabricated as shown in Figure 4. In order to set the desired temperature, the bulb was inserted into the temperature control bath with the stopcock open. The bath was brought approximately to the desired temperature and the stop cock closed. Final temperature adjustment was made by adjusting the tungsten contact height. The control characteristics of this regulator are given in Appendix II.

The outer cylinder was enclosed in a two-inch layer of styrofoam except for the top and a section of the bottom where the magnetic stirrer motor was inserted. The top was covered with a three-eights inch Plexiglas template which was used to position the various parts of the system.

Coolant System

A Podbielniak Flokold unit was used as a source of refrigerated methanol for circulation through the heat sink coils. The insulated storage tank of this unit contained five liters of methanol which were

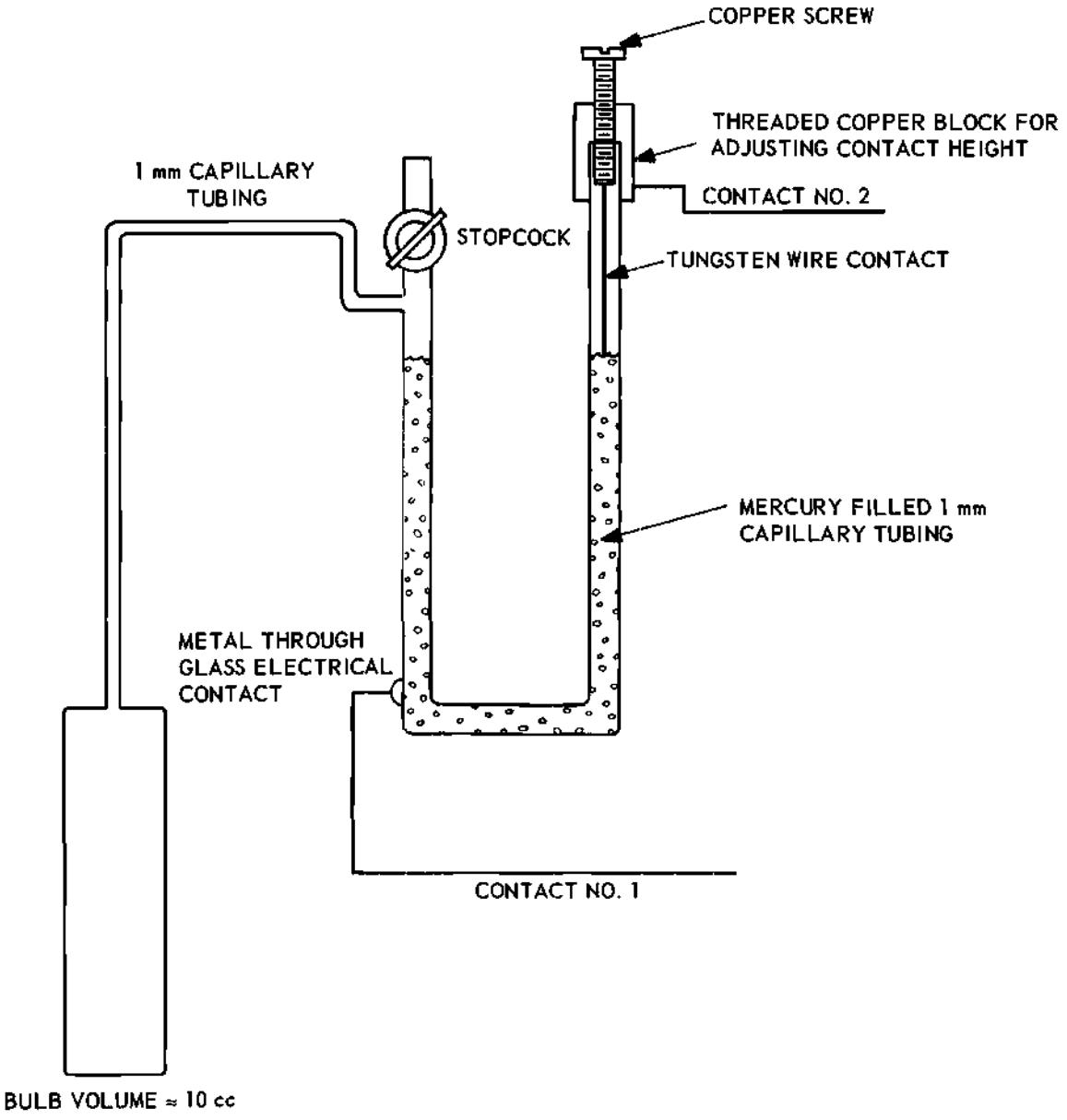

Figure 4. Schematic of Gas Thermoregulator.

cooled by a vapor-compression refrigeration unit. A temperature regulator and coolant circulation pump were also provided. Coolant temperatures could be set and controlled over the temperature range of 220° to 298° K. within ± 1.0°K. by this system. The coolant was usually furnished to the bath at a temperature 10° K. colder than the temperature set point.

In order to reach 195° K., the refrigeration system was deactivated and finely crushed dry ice was added to the coolant storage tank. When there was a considerable excess of dry ice on the tank bottom, the coolant was circulated through the heat sink system. Care was taken to insure that powdered dry ice was maintained in the tank throughout an experimental run.

All interconnecting coolant lines were one-quarter inch rubber vacuum tubing with a one inch coating of fiberglass insulation. In the return leg of the coolant system, a copper cooling coil approximately two inches in diameter by three inches high was incorporated as a constant temperature loop for the tracer saturated frits. This copper coil was immersed in methanol contained in a Dewar flask and maintained this methanol bath at a temperature approximately one degree lower than the diffusion bath set point temperature. This section of the coolant return line was called the Frit Conditioning Loop.

Thermocouple Potentiometer System

Rough temperature readings were obtained by using standard mercury or "red liquid" filled thermometers, but the final temperature readings were made with a thermocouple-potentiometer system. Iron-Advance thermocouples were used in conjunction with a Leeds and Northrup K3 potentiometer for this purpose. Calibration procedures used for these thermocouples

are given in Chapter IV. The galvanometer used was of the floating light spot type. An advantage of this type galvanometer was that the actual voltage fluctuations around the set point could be continually observed after the control temperature was reached, requiring only occasional rebalancing of the potentiometer.

Liquid Scintillation Counter

The tracer concentration of the stirred bath samples was monitored by use of a Packard Model 314 EF liquid scintillation spectrometer system. This system gave efficiencies of the order of 20 to 30 percent when used to count tritium-containing samples dissolved in the scintillation solution described in Chapter IV.

A schematic diagram of the system is shown in Figure 5. The samples, photomultipliers, and preamplifiers were contained in a special refrigeration chamber kept at 5° C. to reduce the number of thermal electrons emitted by the photomultipliers. The preamplifiers were located immediately adjacent to the photomultipliers to prevent the pickup of electrical noise which might occur if the preamplifier lead-in lines were long.

The coincidence unit would pass only those pulses which arrived within 2×10^{-7} seconds of one another. This was to eliminate as much of the random electrical noise generated in each separate photomultiplier-amplifier system as was possible.

The energy band-pass width of the analyzer unit could be adjusted to permit discrimination between isotopes on the basis of their different decay energy spectra.

The scaler unit could be set to count for a preset time or a preset number of counts. The total count for each sample was displayed on

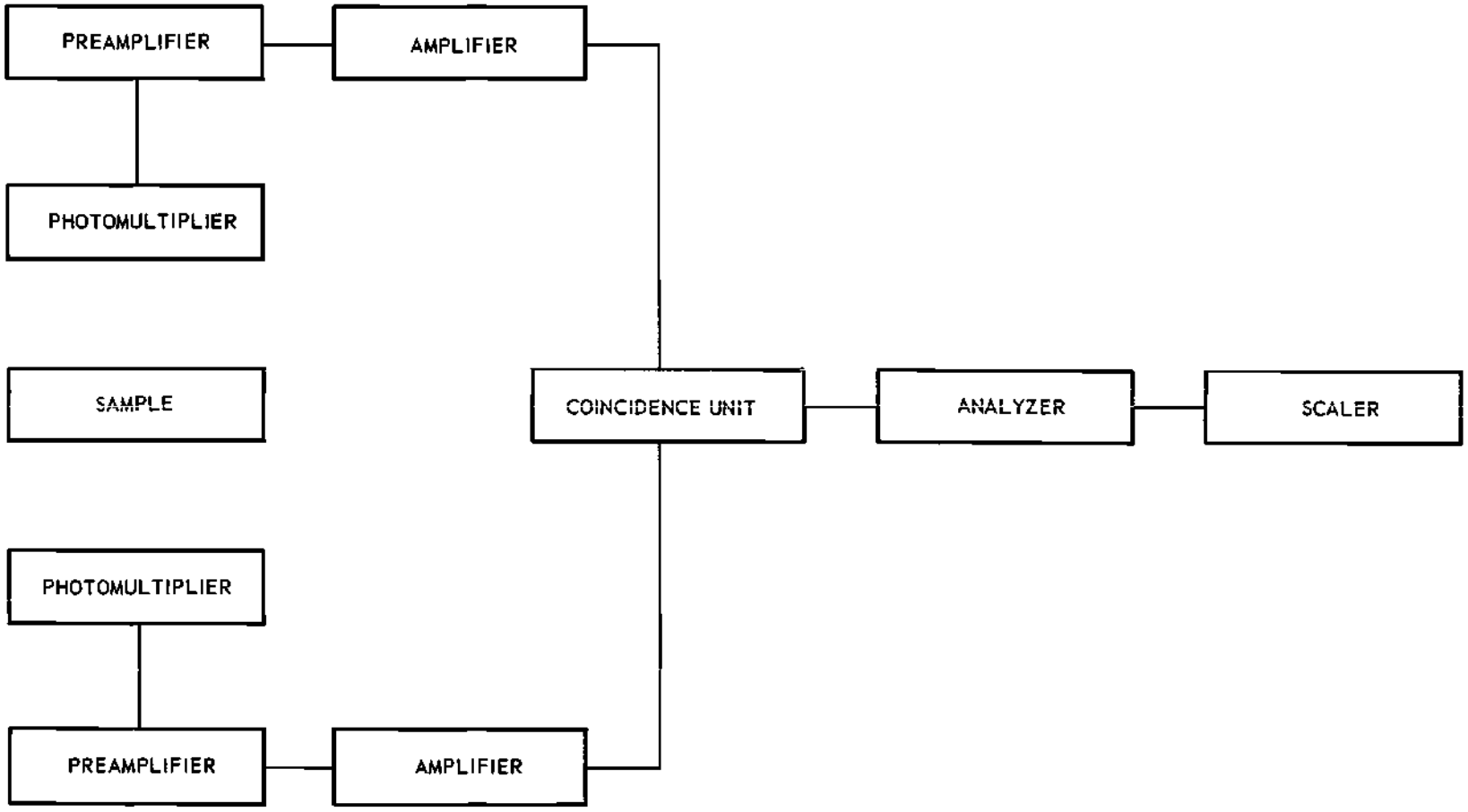

Figure 5. Schematic of Packard 314 EF Liquid Scintillation Counter.

a six decade scaler unit and the time of counting was displayed in one-hundredths of a minute on a four decade scaler unit.

Miscellaneous

The sintered glass frits used in this work were Kimax 30 mm diameter discs with nominal pore size of 4.0 to 5.5 microns. The glass used was K G - 33 which had a reported linear coefficient of expansion of $3.2 \times 10^{-7}/^{\circ}$ C. from 0 to 300° C.

Timer

The timer used for the viscosity determinations and for the experimental runs was an Eastman Kodak spring wound photo timer. A rough check for accuracy was made by comparing the Kodak timer with a synchronous electric motor driven wall clock for a two-hour interval. The Kodak timer was only six seconds slower than the electric clock for this period of time and was used in this condition for all timed operations.

Glassware

Class A volumetric pipets and volumetric flasks were used in order to make the errors in liquid volume measurement as small as possible.

Viscometers

The viscometers used were Cannon-Fenske units which were supplied with a certificate of calibration. The calibration was checked against double distilled water or a certified viscosity oil obtained from the Chemical Sciences Division of the Georgia Institute of Technology Engineering Experiment Station. The calibrations were determined to be correct by these measurements.

Balances

A Westphal balance was used to measure the densities of the various solutions. The unit was capable of measuring density changes as small as 0.0001 g/cc. A Mettler balance was used for general purpose weighing. This unit had a sensitivity of 0.1 mg.

CHAPTER IV

EXPERIMENTAL PROCEDURES

Calibration of the Thermocouples

The thermocouples used in this work were constructed from Anaconda 32 gauge enameled and double glass wrapped copper and Advance (constantan) thermocouple wire. The junction was prepared by carefully cleaning one-half inch ends of each wire, twisting these ends together, and welding them.

The cold junction used for the calibration set points was prepared from double distilled water and ice prepared from distilled water and was kept in a specially cleaned Dewar flask.

The first reference temperature was the sublimation temperature of carbon dioxide under 742 mm Hg pressure. The dry ice was cracked until it was in approximately one-fourth to one-eighth inch pieces and placed in a clean Dewar flask. The thermocouple was placed in the middle of the dry ice chips and a loose fitting stopper placed on the flask. After thirty minutes had elapsed, the potential difference was measured with the Leeds and Northrup K 3 potentiometer.

The second and third reference temperatures were the boiling points of chemically pure methanol and distilled water under 742 mm Hg pressure. One liter of each solvent was placed in a round bottom flask and heated to boiling by a glass mantel heater. The thermocouple was immersed at a position as near to the center of the boiling liquid as possible.

These measured electromotive force (EMF) data points were fitted to a polynomial equation in temperature and a table of EMF versus temperature calculated from this equation is found in Appendix I. EMF values calculated from this equation show excellent agreement with values reported by Edwards (21) who used wire from these same spools in his work.

Density Determination

The densities of the eight solutions were each measured at several temperatures by means of a Westphal balance. This instrument was furnished with a 10 cm^3 quartz float which had been calibrated for use at 20° C. The buoyant force of the liquid on the float which was totally immersed in the liquid was used in making the density determination. In order to make an estimate of the error in calibration which would exist at temperatures other than 20° C., several factors were considered. The linear coefficient of expansion for fused silica was given as 2.56×10^{-7} $/^\circ$ K. for the temperature range -191° to 16° C. (22). The coefficient of volume expansion was estimated as equal to three times the linear coefficient, or $7.68 \times 10^{-7}/^\circ$ K. For the float volume of 10 cm^3 and a temperature change of 100° K., the calibration shift is

$$10\ cm^3 \times 7.68 \times 10^{-7}/^\circ\ K. \times 100^\circ\ K. = 7.68 \times 10^{-4}\ cm^3 \qquad (4.1)$$

As the error was less than 10^{-3} cm^3 for measurements taken under conditions furthest from the calibration point, no correction terms were applied to the readings taken.

The sample to be measured was placed into a pyrex sample holder

which had been cleaned by rinsing twice with the sample solution just prior to the measurement. The sample and the quartz float were allowed to reach temperature equilibrium before the density measurements were recorded. Equilibrium was said to be reached when no further change was necessary to balance the system after a five minute interval. For determinations at reduced temperatures, a cover with a small hole for the float suspension wire was placed over the sample to prevent moisture from condensing into the sample. Elevated temperatures also required a cover to prevent evaporation from the system.

A check on the overall density determination system was made by measuring the density of distilled water at several temperatures. Measured values were found to agree closely with those found in the literature. The measured data points were fitted to a polynomial equation in temperature by the method of least squares to obtain the density table given in Appendix III.

Viscosity Determination

In order to study the effect of viscosity as a parameter in the diffusion equation, the solution viscosity of all eight solvent-solute systems was measured as a function of temperature. The Cannon-Fenske viscometers were prepared for each run by rinsing first with acetone, then twice with the solution whose viscosity was to be determined. The proper amount of solution was then drawn into the viscometer and the viscometer placed into the constant temperature bath to reach equilibrium. The time required to reach equilibrium was usually 15 minutes or less. When the variation in the time of fall of the meniscus on two separate runs made

five minutes apart was less than one second, equilibrium was assumed to have been reached and the times of fall recorded.

The constant temperature bath used for the diffusion runs was used in the viscosity determinations. The same temperature control standard, i.e., a maximum fluctuation of $\pm$ 0.5° K. around the set point, was also used in the viscosity measurements.

The calibration constants of the viscometers are shown in Table 2. These constants were checked by comparing values determined for the viscosity of water, methanol, and acetone with these viscometers at several temperatures with values found in the literature. Agreement between these values was within one percent for each viscometer.

Effect of Temperature on the Viscometer Constant

The Hagan-Poiseuille equation

$$Q = \frac{\pi \Delta P}{8\mu} (r^4)(\frac{1}{L}) \qquad (4.2)$$

when differentiated with respect to temperature gives

$$\frac{dQ}{dT} = \frac{\pi \Delta P}{8\mu} \left[4 r^3(\frac{1}{L}) \frac{dr}{dT} - \frac{1}{L^2} (r^4) \frac{dL}{dT} \right] \qquad (4.3)$$

For pyrex, the coefficient of linear thermal expansion is 3.25×10^{-6} /° K. (23) and therefore

$$\frac{dr}{dT} = 3.25 \times 10^{-6} \text{ r/° K.} \qquad (4.4)$$

Table 2. Viscometer Characteristics

Identification Number	Nominal Size	Calibration Constant Centistokes/sec
J 688	25	0.002018
J 891	50	0.002973
J 376	100	0.01094

$$\frac{dL}{dT} = 3.25 \times 10^{-6} \text{ L/}^{\circ} \text{ K.} \qquad (4.5)$$

Substituting equations 4.4 and 4.5 into equation 4.3 gives

$$\frac{dQ}{dT} = \frac{\pi \Delta P}{8\mu} (9.75 \times 10^{-6})(\frac{r^4}{L}) \qquad (4.6)$$

Therefore, for the same pressure force and viscosity, the ratio

$$\frac{dQ}{Q} = 9.75 \times 10^{-6} \, dT \qquad (4.7)$$

which shows a variation of less than one-tenth percent for a 100 degree temperature change. For this reason, no correction factors were applied to the viscometer calibrations.

The conversion from centistokes to centipoises was made by dividing the measured kinematic viscosity by the measured density at each temperature. A table of viscosity versus temperature obtained from fitting the measured data points to a polynomial equation in temperature is found in Appendix IV.

Preparation of Diffusion Solutions

Chemicals Used

The solvents used in this work were obtained from Union Carbide Chemicals Company. The minimum purity specified by Union Carbide and the purity of the materials actually furnished as determined by use of a Perkin Elmer model 154 D gas chromatography unit are given in Table 3.

Table 3. Diffusion Solvent Purities

Material	Specified Purity (wt.%) Ref. (24)	Determined Purity by Gas Chromatography (mole%)
Methanol	99.5	99.8
Acetone	99.5	99.8
Methyl ethyl ketone	98.0	99.6
Methyl propyl ketone	95.0	99.3
Methyl isobutyl ketone	99.0	99.1
Methyl amyl ketone	95.0	96.4 / 98.7*

*After distillation

The two figures given for methyl n-amyl ketone represent, respectively, the purity of the material as received and as purified by distillation. The tritium-labeled methanol was furnished by Nuclear Chicago, Inc. with an activity level of 25 mc/mm and was specified as being of "reagent quality." This material was diluted to an activity level of 50 mc/ml with Union Carbide methanol prior to being used.

The tritiated water was furnished by Atomic Accessories, Inc. with an activity level of 100 mc/ml and was used as furnished. The water was also specified as being of "reagent quality." Due to the complications involved in analysis of radioactive materials, these chemicals were used as received with no chemical analysis performed.

Concentrations and Activity Levels

Two different solution concentrations were used in this work, 0.111 molar solutions with water as the solute in ATN, MEK, and MeOH, and 0.0991 molar solutions with methanol as the solute in ATN, MEK, MPK, MiBK, and MAK. The solute concentrations were kept low in order to minimize the non-ideality and concentration effects on the diffusion coefficient. These solutions were easily prepared, as they contained 2.0 and 4.0 ml of solute per liter of solution at 20° C. respectively.

Non-tracer containing solutions were prepared in one liter volumetric flasks from one to two hours prior to being used. Volumetric pipets were used to transfer and measure the solute. The tracer-labeled solutions were prepared in 50 ml quantities, using pipets for the solvent and Aloe ultra-micro volumetric pipets for the solute. These tracer-labeled solutions were kept for extended periods of time by sealing the storage bottles with polyethylene caps.

All tritium containing solutions were prepared to contain a tracer concentration of 0.20 mc/ml. This was checked by counting the activity levels of several of the labeled solutions.

Scintillation Solution Preparation

The solvent used for the liquid scintillation solution was 1,4-dioxane furnished by Union Carbide Chemicals Company. Table 4 gives the properties of the material as received and used compared with the properties of pure 1,4-dioxane. The solutes, napthalene, 2,5-diphenyloxazole (PPO), and 1,4-bis-2-(5-phenyloxazolyl)-benzene (POPOP), were furnished by Packard Instrument Company and were classified as "Scintillation Grade."

The scintillation solution was prepared by dissolving seven grams of PPO, 0.3 grams of POPOP, and 100 grams of napthalene in enough 1,4-dioxane to make one liter of solution. This scintillation solution has been reported to be one of the most efficient solutions available for use in counting tritium-containing systems(25).

Frit Preparation and Saturation

The sintered glass frits were prepared for saturation by forcing 40 ml of pure acetone through each of them in order to remove any residues from previous runs. They were then placed in an oven held at 100° C. for at least eight hours. No further weight loss could be detected in frits dried for longer times on a laboratory balance sensitive to 0.1 mg.

A frit which had been cleaned and dried was placed in the tracer solution at least 48 hours prior to being used. The purpose of this was to insure full saturation of the frit. No weight gain was detectable for frits immersed for longer periods of time. Frits which were wet from a

Table 4. Scintillation Solvent Properties (1,4-Dioxane)

Measured Material Properties		Pure Material Properties* (24)	
Refractive Index	Specific Gravity	Refractive Index	Specific Gravity
20° C.	$20/20^{\circ}$ C.	20° C.	$20/20^{\circ}$ C.
1.4222	1.0358	1.4224	1.0356

previous run with the same solvent-solute system would generally reach saturation by diffusion in 12 hours. This could be checked by the equilibrium tritium concentration of the run in which the frit was used. Low equilibrium count rate indicated that the frit was not properly saturated and longer saturation times were allowed for later runs.

Attaining Constant Temperature

At the beginning of an experimental run, one liter of sample solution was placed in the sample container of the constant temperature bath and the control temperature was set. At least one hour was allowed for the system to reach temperature equilibrium. During this time, the temperature fluctuations were monitored with the thermocouple-potentiometer system and any necessary adjustments were made.

The most common adjustments for the constant temperature bath, with the exception of set point changes, were regulation of the coolant flow rate and of the heater power input so that the heater on and off times were approximately equal. This adjustment had a marked effect on limiting the range of temperature fluctuations around the set point. When the maximum deviations were consistantly less than 0.5° K., the temperature control was considered satisfactory.

The solution containing the tracer-labeled solute and the saturated frits was also brought to operating temperature during this time by being placed in the frit conditioning loop. In this case, temperature fluctuations of $\pm 2^{\circ}$ K. were allowed. This variation was found to have no noticeable effect on the diffusion coefficient when, by mistake, a run was made with the frit solution not preconditioned and 20° K. warmer than the bath

temperature. Any effects which may have occurred took place in the very short time stages of the diffusion where no measurements were taken. Duplicate runs made with the frit solution at the proper temperature gave the same final result. The ± 2.0° K. tolerance was maintained for the frit solution throughout the work in order to minimize any possible error.

The Experimental Run

After the temperature had equilibrated, the sintered glass frit was removed from the tracer solution with long tweezers, blotted quickly on both sides with a paper towel to remove surface drops, and placed in the frit holder. The frit and holder assembly were then inserted into the sample solution and the timer was started. One ml samples of the stirred bath were taken at predetermined times by use of an automatic pipet and were placed in numbered polyethylene liquid scintillation bottles containing 10 ml of the dioxane base scintillation solution.

The first series of samples taken covered the time period during which the tracer concentration of the stirred bath was changing rapidly. When this period was over, it was necessary to wait for the stirred bath to reach an equilibrium tracer concentration. The time required to reach equilibrium varied from 45 minutes to 24 hours for the systems and temperatures studied. Three samples of the equilibrium mixture were taken for a more accurate determination of the equilibrium tracer concentration. At least two experimental runs were made at each condition.

Sample Counting

The samples were taken to the radioisotope counting room in the Georgia Institute of Technology Nuclear Research Center for counting as

soon as possible after completion of an experimental run. A period of more than 12 hours was not allowed to elapse before the samples were counted. This was necessary in order to prevent erroneous readings due to the evaporation of the tracer labeled component. The polyethylene liquid scintillation bottles could not maintain a vapor-tight seal for extended periods of time.

The samples were placed in the cold chamber of the liquid scintillation counter and allowed to cool to the equipment temperature of 5.0° C. The purpose of this reduced temperature, as previously mentioned, was to eliminate as much electrical "noise" from the counting rate as possible without freezing the scintillation solution.

The liquid scintillation counter was set for the best counting conditions for tritium and a system blank, containing 10 ml of scintillation solution and one ml of non-tracer containing diffusion solution, was run. The blank was used to determine the background rate of the system at the start and at the end of a counting session.

Each sample was counted for three minutes and the counts per minute, after being corrected for background rate, were recorded. One of the equilibrium samples was counted for ten minutes to check for any statistical error in the count rate. In no case was this error found to be significant. The corrected count rates for a typical experimental run ranged from 10,000 to 60,000 counts per minute.

Diffusion Data Treatment

The count rates (C_t) observed during the period when the tracer concentration was increasing rapidly were divided by the equilibrium

count rate (C_∞) and the quotient subtracted from unity. This is represented by

$$R_t = (1 - C_t/C_\infty)$$

where R_t is a dimensionless number. By plotting log R_t versus the time associated with it, a straight line was obtained with a slope proportional to the diffusion coefficient, D.

The criterion for acceptance of a set of dual runs was mutual agreement within ten percent. If this requirement was not satisfied, an additional pair of runs was made.

CHAPTER V

EXPERIMENTAL RESULTS AND DISCUSSION

Calibration of the Thermocouples

The sublimation temperature of solid carbon dioxide under 742 mm Hg pressure was calculated to be 194.52° K. from the data of Giague and Egan (26). The relative EMF measured at this temperature was -2.632 millivolt. The boiling point of methanol under 742 mm Hg pressure was reported to be 337.05° K. (27). This corresponded to a relative EMF of 2.505 millivolt. The boiling point of water under 742 mm Hg has been given as 372.48° K. (28). The measured EMF for this point was 4.030 millivolts.

These data points were fitted to a polynomial equation by a least squares curve fitting procedure and the resulting equation was

$$EMF = -7.0730 + 0.0151931T + 3.9250514 \times 10^{-5}T^2 \qquad (5.1)$$

Table 5 gives a comparison of values calculated from equation 5.1 and values reported by Edwards (21) who used wire from the same spools in preparing his thermocouples. The maximum difference between the values represents only 0.2° K. A table of values of the calculated EMF versus temperature for the entire temperature range studied is presented in Appendix I.

Table 5. Comparison of EMF Calculated from Equation 5.1 with Values Reported by Edwards (All values in millivolts)

T^{o} K.	Eqn. 5.1	Edwards	Δ
293	0.748	0.747	+.001
303	1.134	1.132	+.002
313	1.527	1.527	+.000
353	3.181	3.180	+.001
363	3.614	3.608	+.006

Density Measurements

The measured values for the densities of the solutions used as a function of temperature are shown in Table 6. Figures 6, 7, and 8 show the measured densities plotted versus temperature. The measured data points were fitted to a polynomial equation in temperature by a least squares method and the following equations for the solution densities as a function of temperature were derived.

Solutions Containing 0.111 Molar H_2O

$$\rho_{MeOH} = 1.2060 - 2.7214 \times 10^{-3}T + 6.9977 \times 10^{-6}T^2 - 8.6262 \times 10^{-9}T^3 \quad (5.2)$$

$$\rho_{ATN} = 1.1834 - 2.1510 \times 10^{-3}T + 4.5163 \times 10^{-6}T^2 - 5.9594 \times 10^{-9}T^3 \quad (5.3)$$

$$\rho_{MEK} = 1.0136 - 5.2477 \times 10^{-5}T - 3.7418 \times 10^{-6}T^2 + 5.1087 \times 10^{-9}T^3 \quad (5.4)$$

Solutions Containing 0.0991 Molar MeOH

$$\rho_{ATN} = 1.3086 - 3.6692 \times 10^{-3}T + 1.0506 \times 10^{-5}T^2 - 1.3686 \times 10^{-8}T^3 \quad (5.5)$$

$$\rho_{MEK} = 1.0071 + 1.5266 \times 10^{-5}T - 3.9933 \times 10^{-6}T^2 + 5.4306 \times 10^{-9}T^3 \quad (5.6)$$

$$\rho_{MPK} = 1.3616 - 4.9456 \times 10^{-3}T + 2.0109 \times 10^{-5}T^2 - 4.2243 \times 10^{-8}T^3$$

$$+3.1331 \times 10^{-11}T^4 \quad (5.7)$$

Table 6. Measured Densities of Solutions Used gm/cm^3

	0.111 Molar Solutions of H_2O in			0.0991 Molar Solutions of MEOH in				
T° K.	ATN	MEK	MEOH	ATN	MEK	MPK	MiBK	MAK
195	.8920	.8995	.8780	.8918	.8990	.8945	.8820	
251	.8340	.8455	.8270	.8330	.8450	.8435	.8355	.8480
273	.8110	.8245	.8103	.8120	.8247	.8250	.8178	.8315
293	.7913	.8055	.7918	.7910	.8050	.8071	.8010	.8150
323	.7589	.7785	.7665	.7585	.7785	.7798	.7764	.7910
353						.7500		
368							.7327	.7520
423								.7030

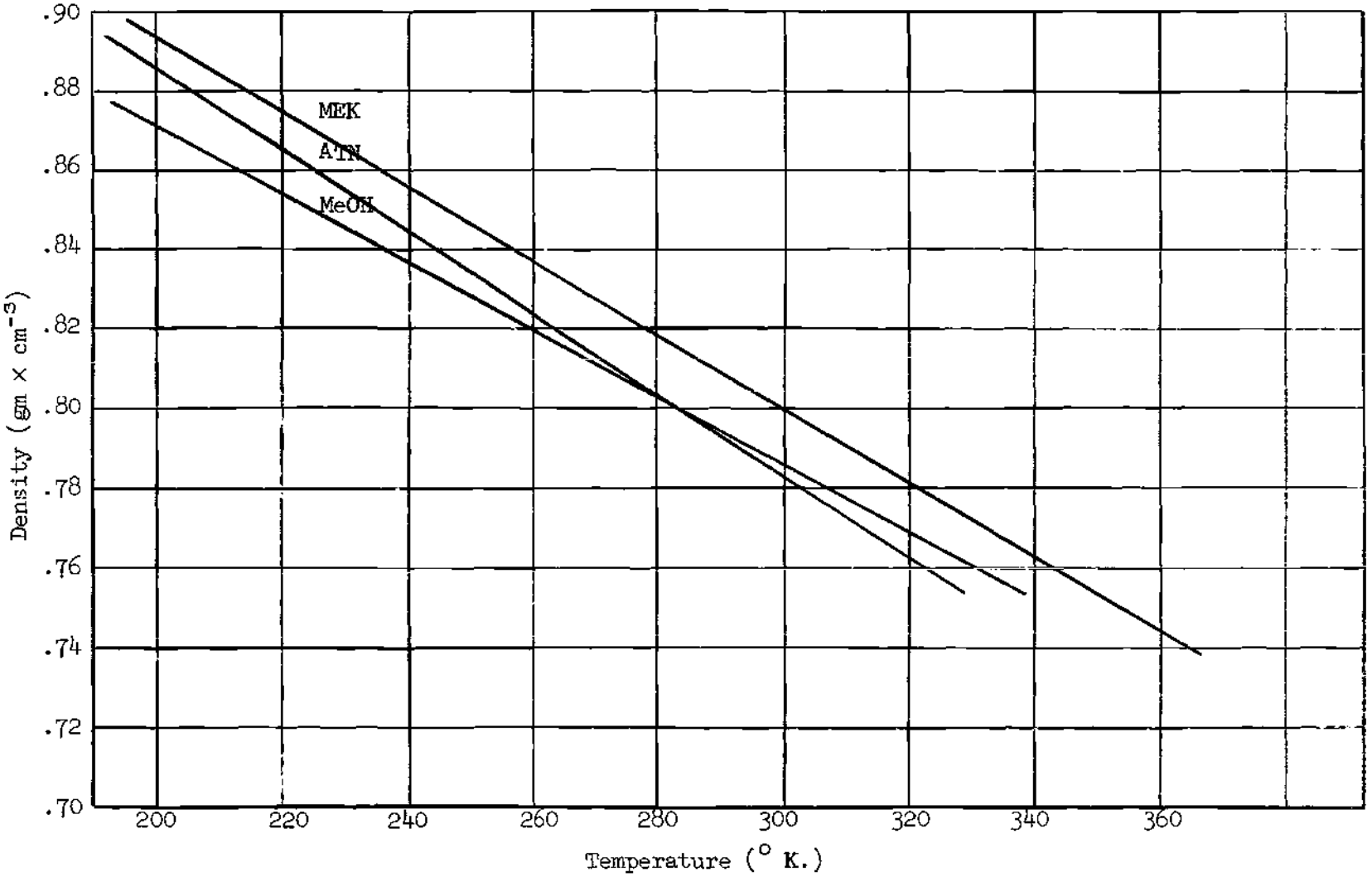

Figure 6. Density of Solutions Containing Water as Solute Versus Temperature

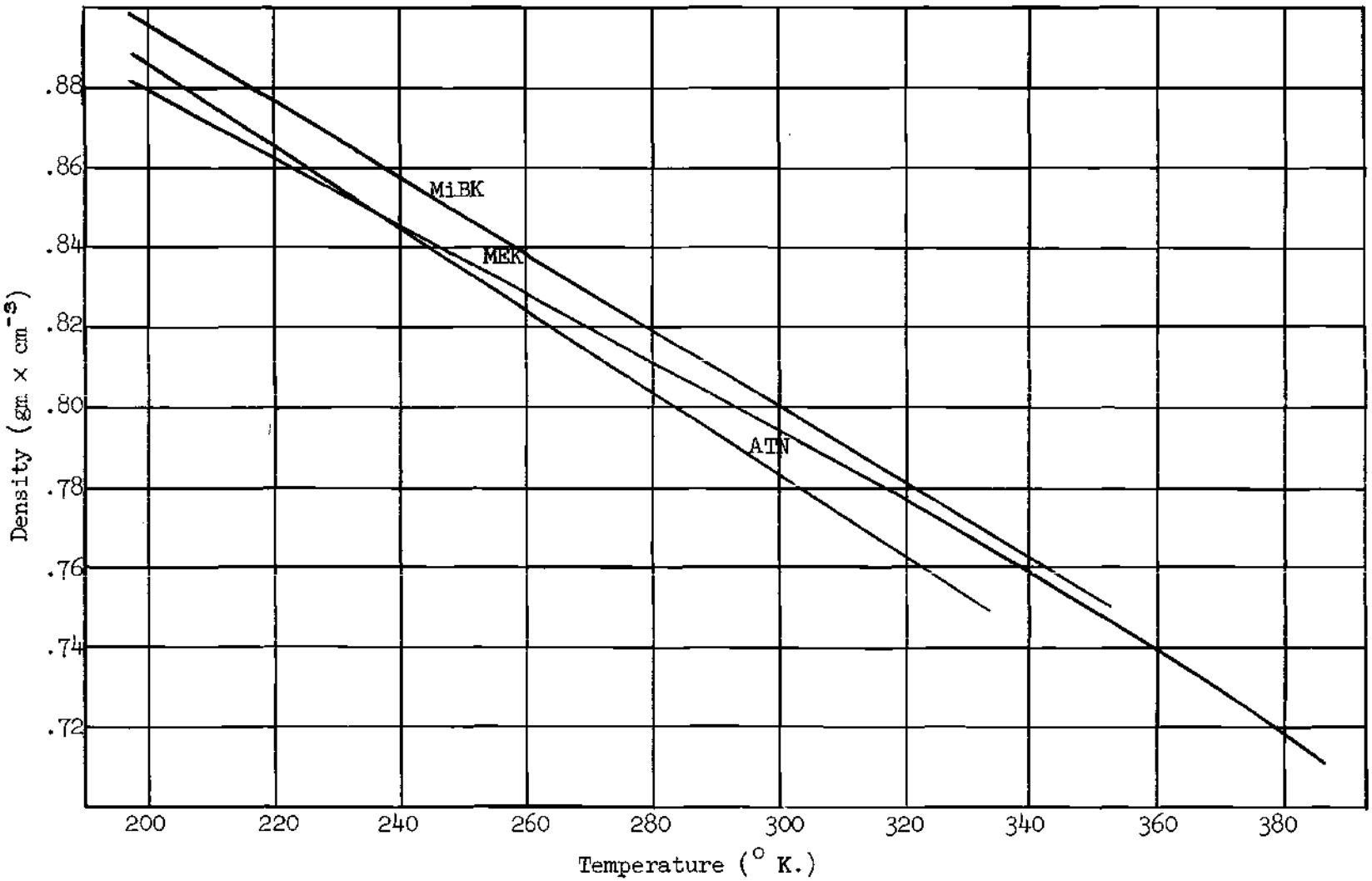

Figure 7. Density of Solutions Containing Methanol as Solute Versus Temperature

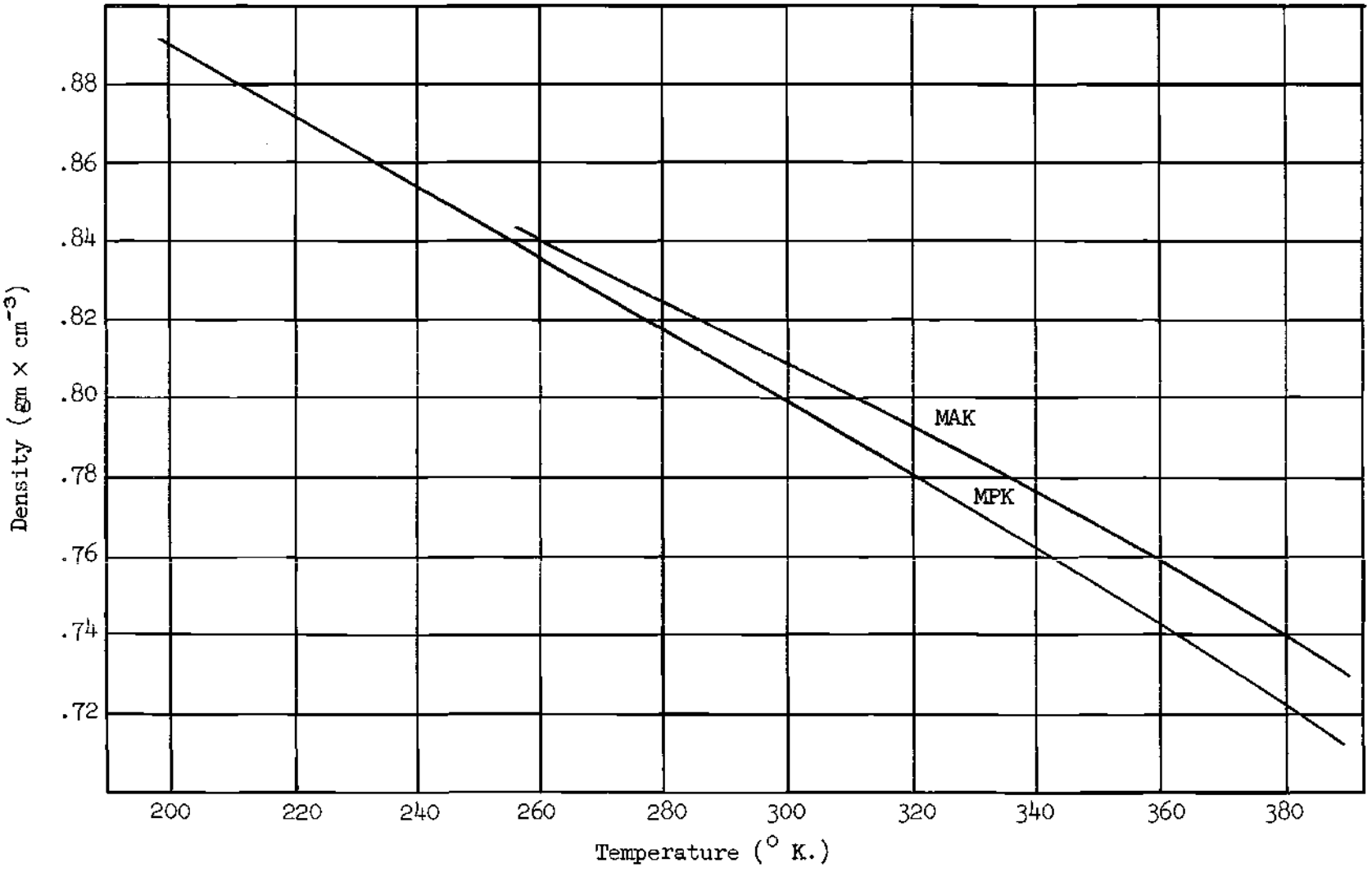

Figure 8. Density of Solutions Containing Methanol as Solute Versus Temperature

$$\rho_{MiBK} = 0.7272 + 4.1756 \times 10^{-3}T - 2.9432 \times 10^{-5}T^2 + 7.6237 \times 10^{-8}T^3$$

$$-7.3323 \times 10^{-11}T^4 \qquad (5.8)$$

$$\rho_{MAK} = 1.0832 - 1.5647 \times 10^{-3}T + 4.9126 \times 10^{-6}T^2 - 1.2108 \times 10^{-8}T^3$$

$$+9.9665 \times 10^{-12}T^4 \qquad (5.9)$$

Table 7 compares the measured values with values taken from the literature. It can be seen that in no case is the error as great as one percent. A table of the calculated densities of all eight solutions versus temperature is given in Appendix III.

Viscosity Measurements

The measured values for the viscosities of the various systems studied as a function of temperature are shown in Table 8. Figures 9 and 10 show the measured viscosities plotted as a function of temperature. The measured data points were fitted to polynomial equations in temperature by a method of least squares and the following viscosity-temperature equations were developed:

Solutions with 0.111 Molar H_2O

$$\text{Log } \mu_{MeOH} = 2.1902 - 0.41727 \times 10^4/T + 0.13751 \times 10^7/T^2$$

$$-0.11360 \times 10^9/T^3 \qquad (5.10)$$

Table 7. Comparison of Average Measured Densities with Values from the Literature (gm/ml^3)

	T° K.	Measured values	Lit. value	Ref.
Acetone	293	.7911	.7905	(27)
MEK	293	.8053	.8049	(27)
MPK	293	.8071	.8064	(27)
MiBK	293	.8010	.8032	(27)
MAK	293	.8150	.8154	(27)
MEOH	293	.7918	.7912	(27)
Water	273	.9999	.9998	(29)
"	293	.9987	.9982	(29)
"	323	.9880	.9880	(29)
"	353	.9750	.9718	(29)
"	368	.9650	.9619	(29)

Table 8. Measured Viscosities in Centipoises of Solutions Used

T° K.	ATN	MEK	MEOH	ATN	MEK	MPK	MiBK	MAK
195	1.52	2.60	5.28	1.48	2.501	3.96	6.47	
251	.543	.717	1.24	.535	.707	.927	1.15	1.84
273	.399	.508	.786	.400	.505	.626	.741	1.10
293	.321	.400	.585	.320	.401	.495	.575	.813
323	.245	.303	.398	.246	.303	.367	.414	.553
353						.278		
368							.275	.356
423								.236

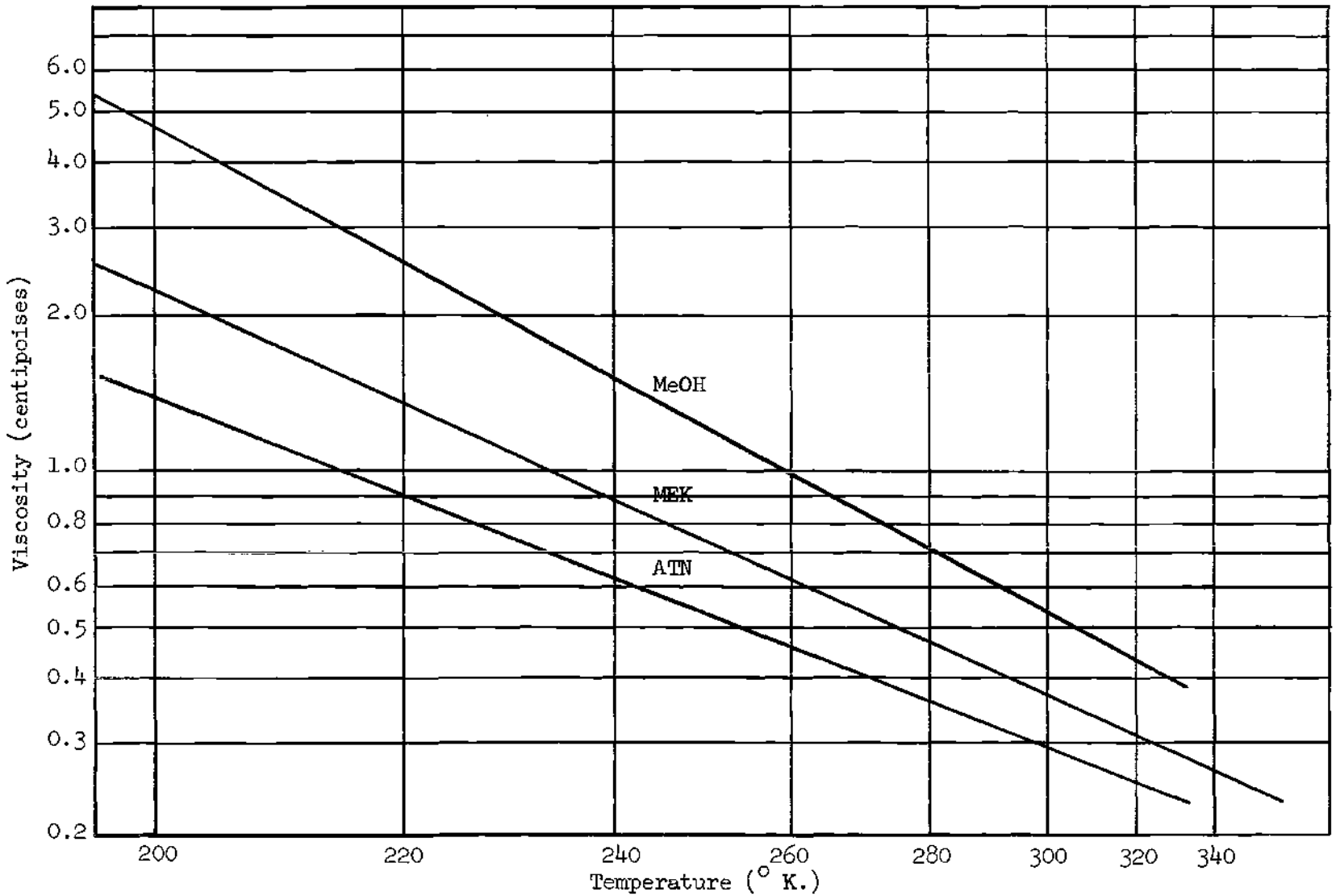

Figure 9. Viscosity of Solutions with Water as Solute Versus Temperature

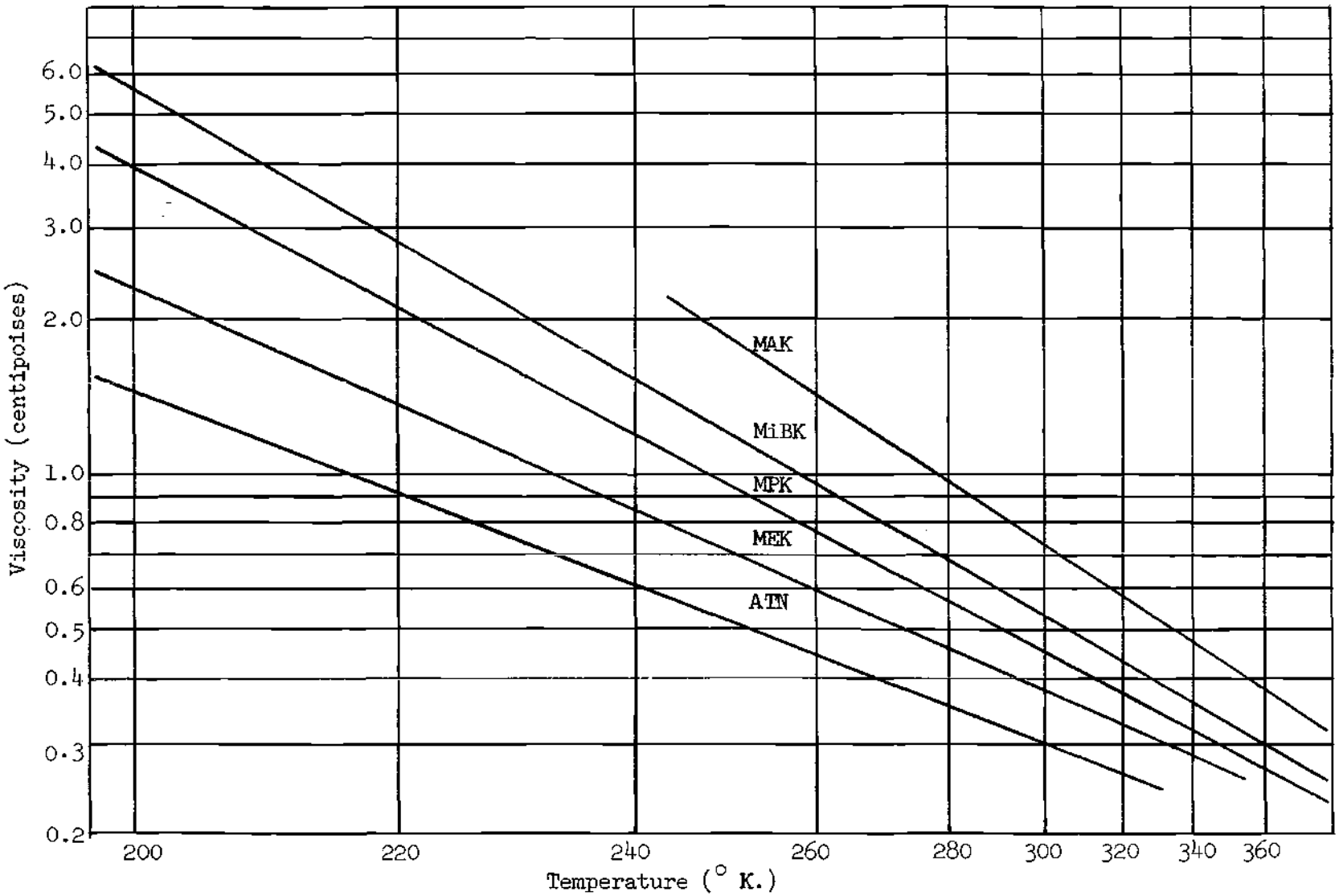

Figure 10. Viscosity of Solutions with Methanol as Solute Versus Temperature

$$\text{Log } \mu_{ATN} = -0.5403 - 0.18998 \times 10^4/T + 0.70136 \times 10^6/T^2$$

$$-0.57485 \times 10^8/T^3 \qquad (5.11)$$

$$\text{Log } \mu_{MEK} = 0.6256 - 0.25616 \times 10^4/T + 0.82973 \times 10^6/T^2$$

$$-0.62048 \times 10^8/T^3 \qquad (5.12)$$

Solutions with 0.0991 Molar MeOH

$$\text{Log } \mu_{ATN} = -1.4725 - 0.11503 \times 10^4/T + 0.50687 \times 10^6/T^2$$

$$-0.41348 \times 10^8/T^3 \qquad (5.13)$$

$$\text{Log } \mu_{MEK} = -0.4775 - 0.16946 \times 10^4/T + 0.60953 \times 10^6/T^2$$

$$-0.44184 \times 10^8/T^3 \qquad (5.14)$$

$$\text{Log } \mu_{MPK} = -46.0481 + 0.47342 \times 10^5/T - 0.18889 \times 10^8/T^2$$

$$+0.33586 \times 10^{10}/T^3 - 0.21913 \times 10^{12}/T^4 \qquad (5.15)$$

$$\text{Log } \mu_{MiBK} = -35.5043 + 0.36349 \times 10^5/T - 0.14605 \times 10^8/T^2$$

$$+0.26240 \times 10^{10}/T^3 - 0.17183 \times 10^{12}/T^4 \qquad (5.16)$$

$$\text{Log } \mu_{MAK} = 10.9848 - 0.19636 \times 10^5/T + 0.10611 \times 10^8/T^2$$

$$-0.23901 \times 10^{10}/T^3 + 0.20076 \times 10^{12}/T^4 \qquad (5.17)$$

Table 9 compares the measured viscosities with values found in the literature. The average error appears to be on the order of three percent with an occasional six percent difference. Part of this discrepancy is attributed to the fact that the viscosity is an exponential function of temperature, and small fluctuations in temperature cause noticeable percentage changes in the value of this function. At 293° K., a one-half degree change in temperature corresponds roughly to a one percent change in the viscosity for all eight solutions studied. There is also some difference between values reported by different sources as can be seen from Table 9.

The measured values and values calculated by equations 5.10 through 5.17 were used in the comparison of estimation methods for the diffusion coefficients presented in Chapter VI. Since most of the estimation methods incorporate viscosity as a parameter, an error in viscosity will have little effect on the comparison of the methods. A table of calculated viscosities for the eight solutions as a function of temperature is presented in Appendix IV.

Calibration of the Frits

In order to establish the frit coefficient for each frit to be used, it was necessary to know the value of the diffusion coefficient for a system which could be used as a calibration standard. The average

Table 9. Comparison of Measured Viscosities with Values from the Literature

Solvent	T° K.	Measured	Lit. Value	Ref.
ATN	251	.543	.510	(30)
	273	.399	.399	(30)
			.401	(31)
	293	.321	.331	(31)
	323	.245	.256	(31)
MEK	273	.507	.528	(32)
			.522	(31)
	293	.400	.416	(31)
			.428	(32)
	323	.303	.312	(31)
MPK	273	.626	.647	(31)
	293	.495	.506	(31)
	323	.367	.372	(31)
	353	.278	.287	(31)
MEOH	273	.786	.82	(30)
	293	.585	.597	(30)
	323	.398	.403	(30)
Water	273	1.785	1.7921	(30)
	293	1.015	1.0050	(30)
	323	0.562	0.5494	(30)
	353	0.370	0.3565	(30)
	368	0.301	0.2994	(30)

value for the self-diffusion coefficient of water at 298° K. as determined from ten values reported in the literature (33) was used for this purpose. Use of this value for D, 2.35×10^{-5} cm^2/sec, gives the following equation for the determination of the frit constant:

$$\frac{\Delta \log (1 - C_{Bt}/C_{B\infty})}{\Delta t} \quad \frac{1}{2.35 \times 10^{-5}} = K_F \tag{5.18}$$

or

$$\frac{\text{slope}}{2.35 \times 10^{-5}} = K_F \tag{5.19}$$

Table 10 gives the slopes determined from duplicate runs with each of the five frits used and the corresponding frit coefficients. Since each of the frit coefficients was so close to the average value of 2.68×10^3, this value was used for all experimental runs.

A further check of the frit coefficient was made by measuring the slope for diffusion of methanol in water at 288° K. When this measured slope, 3.58×10^{-2}, was divided by the frit coefficient, a value of 1.33×10^{-5} cm^2/sec was obtained for the diffusion coefficient. This value compared very favorably with the reported value of 1.28×10^{-5} (1).

The Effect of Stirring Rate on Slope Determinations

The possibility that the stirring rate of the diffusion bath could affect the rate of diffusion was studied in a series of experimental runs. The system used for this study was the diffusion of water in methanol at 293° K. The same sintered glass frit was used for each of the runs.

Table 10. Frit Calibration Data

Frit #	Slope $\times 10^{2}$	$K_F \times 10^{-3}$	$K_F - K_{F\ avg}$
1	-6.31	2.68	.00
2	-6.13	2.61	-.07
3	-6.47	2.75	+.07
4	-6.42	2.73	+.05
5	-6.26	2.66	-.03
avg.	-6.32	2.68	

Sum of Square

13.2×10^{-3}

Population Variance

3.30×10^{-3}

Standard Deviation

5.75×10^{-2}

Probable Error Range at 95% Confidence Level

2.67%

Run M 49 had no stirring except for the 30 second period just prior to a sample being taken. Run M 50 had very slow continuous stirring with rapid stirring for the 15 second period prior to sampling the bath. Run M 51 had continuous stirring at a medium speed which just caused turbulence to develop. Runs M 29 and M 30 had continuous rapid stirring with well developed turbulence. Table 11 shows that the slopes measured for these runs did not vary more than 2.92 percent from the average value. Since the rate of stirring appeared to have little effect on the slopes determined in these runs, turbulent stirring was used in all experimental work.

Evaluation of the Sampling and Counting Techniques

Each experimental run required ten or more samples of the diffusion bath to be taken and to be counted for tritium concentration. In order to estimate the accuracy of the measurements, standard deviations were determined for the sampling technique, the counting system, and the overall method (34). The 95 percent confidence level was used throughout this evaluation and the "error range" is one-half the width of this confidence level divided by the sample mean. This value is roughly equal to 2.2 times the coefficient of variation.

Table 12 shows the variations which occurred in 14 one ml samples with a mean activity level of 57,693 counts per minute taken from a constant population. Care was taken to ensure that the samples were taken under conditions similar to those present in an actual experimental run. The confidence belt had an error range of 0.0201 or 2.01 percent.

Table 11. Effect of Stirring Rate on Slope Determination

Run #	Slope	Slope - Avg. Slope	Method
M 49	.0467	-.0012	Fast stir 30 sec. before sample
M 50	.0493	.0014	Slow stir except fast stir 15 sec. before sample
M 51	.0475	-.0004	Medium continuous stirring
M 29	.0476	-.0003	Turbulent stirring
M 30	.0486	.0007	Turbulent stirring

Average Slope
.0479

Population Variance
1.035×10^{-6}

Sum of Squares
4.14×10^{-6}

Standard Deviation
1.017×10^{-3}

Probable Error Range at 95% Confidence Level
5.90%

Table 12. Variations in Samples Taken from the Same Population

Sample #	Count Rate	Δ Count Rate	Δ^2 Count Rate
1	57908	214	45949
2	57496	-197	39062
3	57800	106	11312
4	57284	-409	167806
5	58840	1146	1314136
6	57225	-468	219625
7	57894	200	40143
8	58051	357	127704
9	57214	-479	230056
10	57290	-403	162926
11	58399	705	497529
12	57299	-394	155742
13	58090	396	157099
14	56921	-772	596975

Average Count Rate	Sum Δ^2	Standard Deviation	Population Variance
57693	3766070	538	289697

Part A of Table 13 shows the variations which occurred in twenty activity determinations of one sample with a mean activity level of 56,433 counts per minute. The standard deviation was roughly one-half that which occurred in the previous case where the variance in counting and sampling techniques were both present. The error range in the counting technique for this activity level was 0.00942 or 0.942 percent.

It was assumed that the activity levels of the two previous systems were both equal to approximately 57,000 counts per minute and that the count rate, C, was equal to the product of the sampling technique, A, and the counting technique, B. The error in the sampling technique was determined by use of the relation (35)

$$\frac{dC}{C} = \frac{\Delta A}{A} + \frac{\Delta B}{B} \qquad (5.20)$$

The error range for the sampling technique was determined to be 1.07 percent. This sampling error was assumed to be independent of the activity level of the diffusion bath.

The error range for the counting technique was a function of the activity level and Table 13 shows the variations which occurred in samples taken from activity levels of 57,000, 30,000, and 9,000 counts per minute. Most of the data taken in the experimental runs fell in the 30,000 to 60,000 count per minute range. The counting error ranges for these activity levels were 1.61 and 0.942 percent respectively. The maximum counting error range of 1.61 percent was used in the evaluation of all data except $C_{B\infty}$ where the lower value of 0.942 percent was applied.

Table 13. Variations in Count Rate for One Sample

Sample #	Count Rate	Δ Count Rate	Δ^2 Count Rate
		Part A	
1	56535	99	9940
2	56842	409	167854
3	56742	308	95295
4	56396	- 37	1391
5	56551	117	13853
6	56429	- 4	18
7	56100	-333	111088
8	56741	307	94679
9	56718	284	81034
10	56348	- 85	7276
11	56191	-242	58709
12	56139	-294	86612
13	56638	204	41902
14	55930	-503	253310
15	56174	-259	67236
16	56452	18	349
17	56568	134	18144
18	56289	-204	41738
19	56368	-165	27324
20	56676	242	58903
		Part B	
1	30263	175	30695
2	29883	-204	41943
3	29730	-357	128020
4	30068	- 19	392
5	30135	47	2227
6	30133	45	2043
7	30030	- 57	3340
8	29984	-103	10774
9	30529	441	194657
10	30123	35	1239

Table 13. Variations in Count Rate for One Sample (Concluded)

Sample #	Count Rate	Δ Count Rate	Δ^2 Count Rate
		Part C	
1	9915	265	70331
2	9639	- 10	116
3	9530	-119	14352
4	9682	32	1036
5	9542	-107	11620
6	9633	- 16	282
7	9785	135	18279
8	9529	-120	14592
9	9489	-160	25856
10	9754	104	10857

Part	Average Count Rate	Sum Δ^2	Standard Deviation	Population Variance
A	56433	1236681	255	65088
B	30087	415333	214	46148
C	9649	167325	136	18591

This gave an overall error range of 2.68 percent for the data points and 2.01 percent for $C_{B\infty}$.

The plotted data points represent the term $\log \left[(C_{B\infty} - C_{Bt})/C_{B\infty} \right]$ as a function of time. The argument of the logarithm contains both a difference and a quotient. The estimate of the population variance of the difference may be obtained by the use of the relation (36)

$$s^2 (C_{B\infty} - C_{Bt}) = s^2 (C_{B\infty}) + s^2 (C_{Bt}) \qquad (5.21)$$

The population variance for the difference was then equal to the sum of the population variance for $C_{B\infty}$ and the population variance of a sample C_{Bt} taken at an activity level between 30,000 and 60,000 counts per minute. In most cases this difference population variance lay between 416,000 and 578,000 with standard deviations of 645 and 760 respectively. The maximum difference error range then becomes $1660/(C_{B\infty} - C_{Bt})$. It was evident that this value increased rapidly as C_{Bt} approached $C_{B\infty}$. When $C_{Bt} = 0.50\ C_{B\infty}$, the error range was 5.55 percent, but equaled 13.9 percent when $C_{Bt} = 0.80\ C_{B\infty}$. The overall error range for the argument of the logarithm was 16 percent at $C_{Bt} = 0.80\ C_{B\infty}$ and the value for C_{Bt} was chosen as the maximum value to be used in computing the slopes for the diffusion coefficient evaluation.

Evaluation of the Error in Slope Determination

Eight experimental runs were made with the same frit to determine the variation in slope for the diffusion of water in methanol at 293° K. Table 14 presents the data obtained from these runs. The standard devia-

Table 14. Variance in Slope for Diffusion of Water in Methanol at 293° K.

Slope × 10^4	Δ Slope × 10^4	Δ^2 Slope × 10^8
440	-36.7	1350.5
485	8.2	68.1
507	30.2	915.1
482	5.2	27.6
490	13.2	175.6
476	- .75	.56
450	-26.7	715.6
484	7.2	52.6

Average Slope × 10^4	Standard Deviation × 10^4
476.7	21.73
Sum Δ^2 Slope × 10^8	Population Variance × 10^8
3305.5	472.2

tion is 2.17×10^{-3} and the error range at the 95 percent confidence level is 10.8 percent. The maximum deviation from the average value which actually occurred was 7.74 percent. As each slope used in the computation of diffusion coefficients was determined from the average slope of two runs made under identical conditions, the error range for the average slope was 7.64 percent.

The Calculated Diffusion Coefficients

The average slope determined from at least two experimental runs made at each temperature condition, the diffusion coefficient calculated from the slope and other correlating data for the eight systems observed are presented in Tables 15 and 16. Figures 11, 12 and 13 show that the logarithm of the diffusion coefficient plotted versus temperature gives a definitely curved line. Figures 14 through 21 show that when the diffusion coefficient is plotted versus T/μ, a straight line results for all eight systems. From these results, an equation of the form

$$D = K_{system} (T/\mu)^{1.0} \tag{5.25}$$

is suggested. This form of equation for D is also supported by a wide range of data taken from the literature and given in Appendix V.

As the diffusion coefficient was the product of the experimentally determined fcit constant and the experimentally determined slope, the error range for the diffusion coefficient is taken to be the sum of the error ranges for these two factors or 10.41 percent.

Table 15. Measured Slopes, Calculated Diffusion Coefficients, and Related Data for Systems with Water as the Solute

T^{o} K.	Solvent	- Slope	D × 10^{5}(cm^{2}/sec)	μ (cps.)	T/μ
195	Methanol	.0037	.137	5.21	37.4
233	"	.0133	.495	1.91	122.0
253	"	.0223	.829	1.20	211.0
273	"	.0368	1.37	.809	338.0
293	"	.0484	1.79	.585	501.0
323	"	.0735	2.73	.405	798.0
195	Acetone	.0167	.620	1.50	130.
233	"	.0360	1.34	.726	321.
253	"	.0580	2.15	.526	481.
273	"	.0800	2.98	.399	684.
293	"	.1040	3.87	.319	919.
323	"	.1500	5.58	.245	1320.
195	MEK	.0070	.260	2.56	76.2
233	"	.0263	.977	1.01	230.0
253	"	.0397	1.47	.692	366.0
273	"	.0578	2.15	.508	538.0
293	"	.0778	2.89	.400	733.0
323	"	.1120	4.16	.303	1065.0

Table 16. Measured Slopes, Calculated Diffusion Coefficients, and Related Data for Systems with Methanol as the Solute

T° K.	Solvent	- Slope	$D \times 10^{5}$ (cm^2/sec)	μ (cps.)	T/μ
195	Acetone	.0140	.521	1.46	133
233	"	.0390	1.45	.710	328
253	"	.0500	1.86	.520	486
273	"	.0760	2.83	.400	683
293	"	.1000	3.72	.320	915
323	"	.1370	5.10	.246	1310
195	MEK	.0110	.409	2.46	79
233	"	.0270	1.00	.983	237
253	"	.0410	1.52	.683	371
273	"	.0690	2.57	.507	539
293	"	.0860	3.20	.399	735
323	"	.1430	5.32	.303	1065
195	MPK	.0061	.227	3.96	49
233	"	.0210	.781	1.44	162
253	"	.0370	1.38	.889	285
273	"	.0540	2.01	.630	434
293	"	.0680	2.53	.491	596
323	"	.1080	4.02	.367	880
353	"	.1830	6.80	.278	1270
195	MiBK	.0034	.126	6.36	30
233	"	.0150	.559	1.85	126
253	"	.0250	.930	1.09	232
273	"	.0370	1.38	.747	365
293	"	.0530	1.97	.567	517
323	"	.0830	3.09	.414	781
353	"	.1100	4.09	.316	1115
368	"	.1450	5.40	.275	1340
253	MAK	.0220	.819	1.74	145
273	"	.0310	1.15	1.10	248
293	"	.0520	1.93	.809	362
323	"	.0910	3.38	.558	579
368	"	.1660	6.18	.356	1034

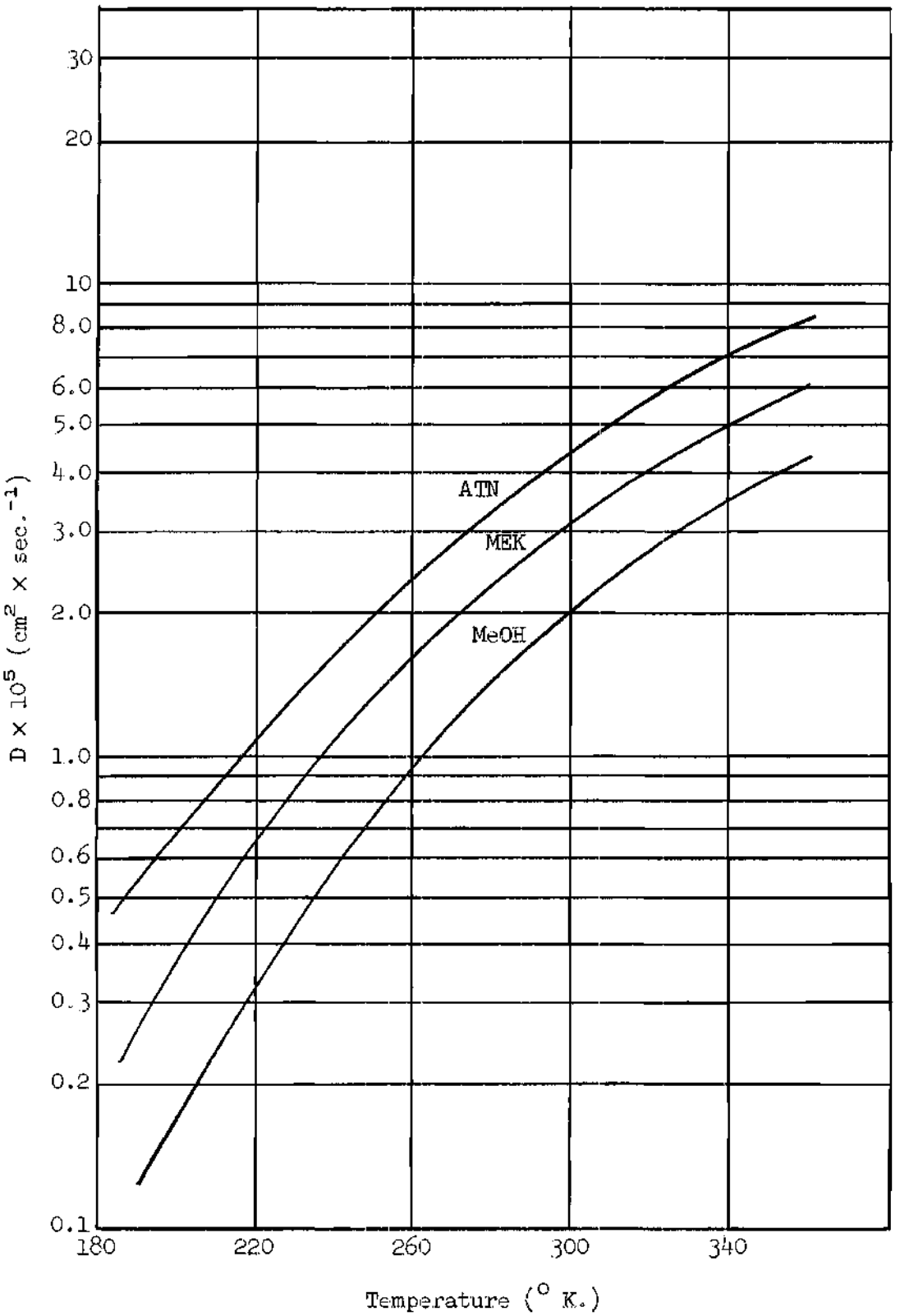

Figure 11. Diffusion Coefficient in T° K. Systems with Water as Solute Versus Temperature

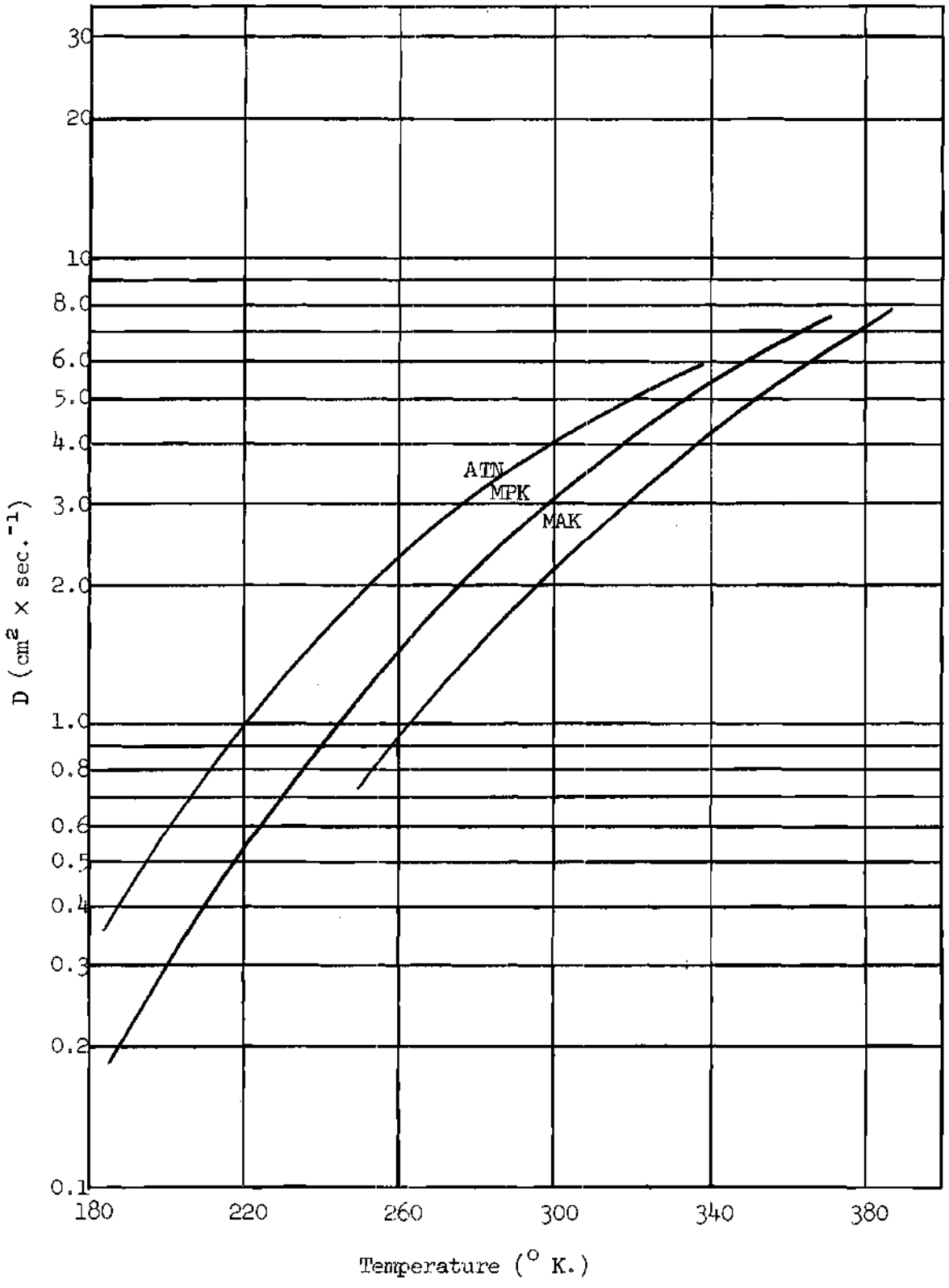

Figure 12. Diffusion Coefficient in Systems with Methanol as Solute Versus Temperature

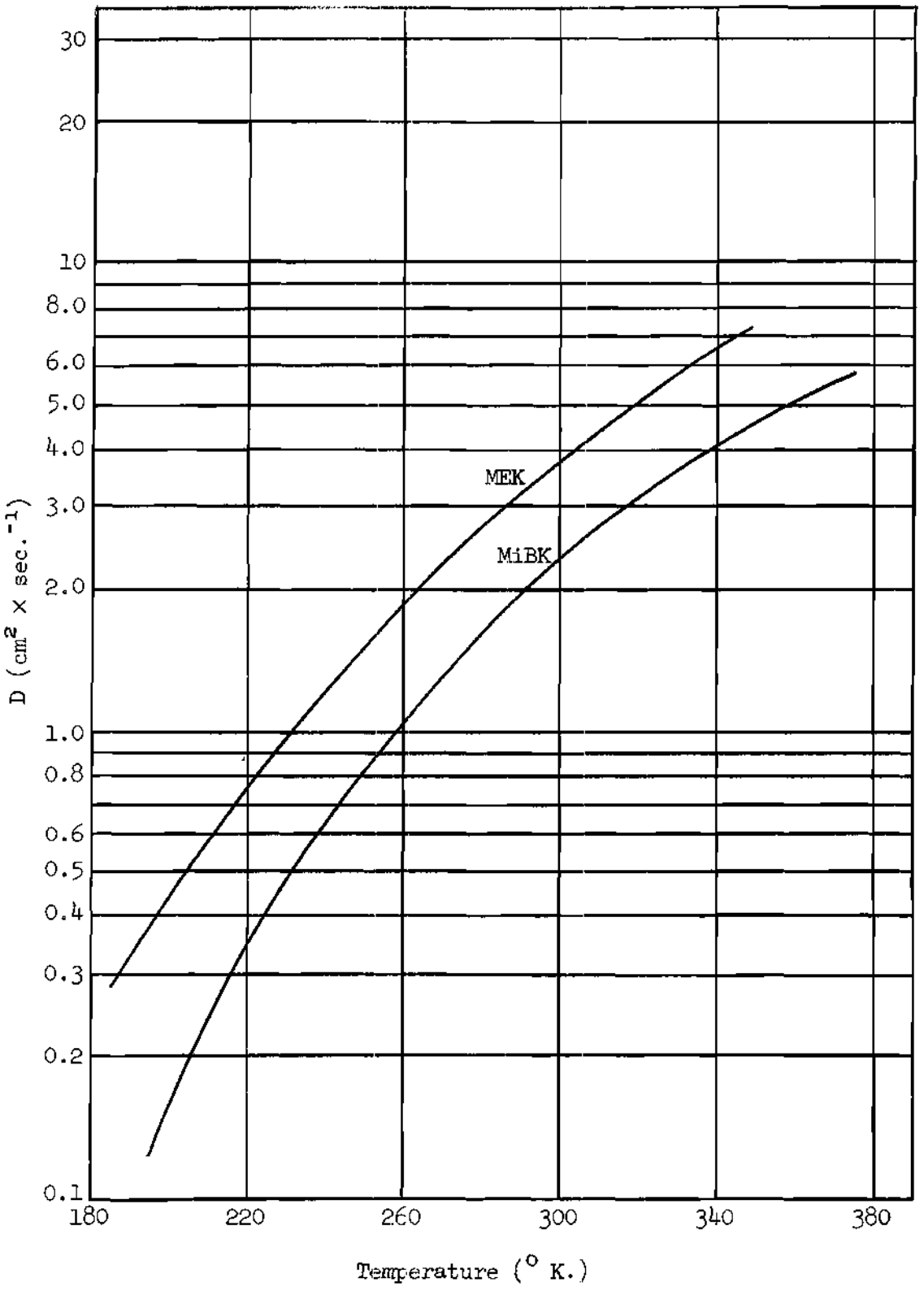

Figure 13. Diffusion Coefficient in Systems with Methanol as Solute Versus Temperature

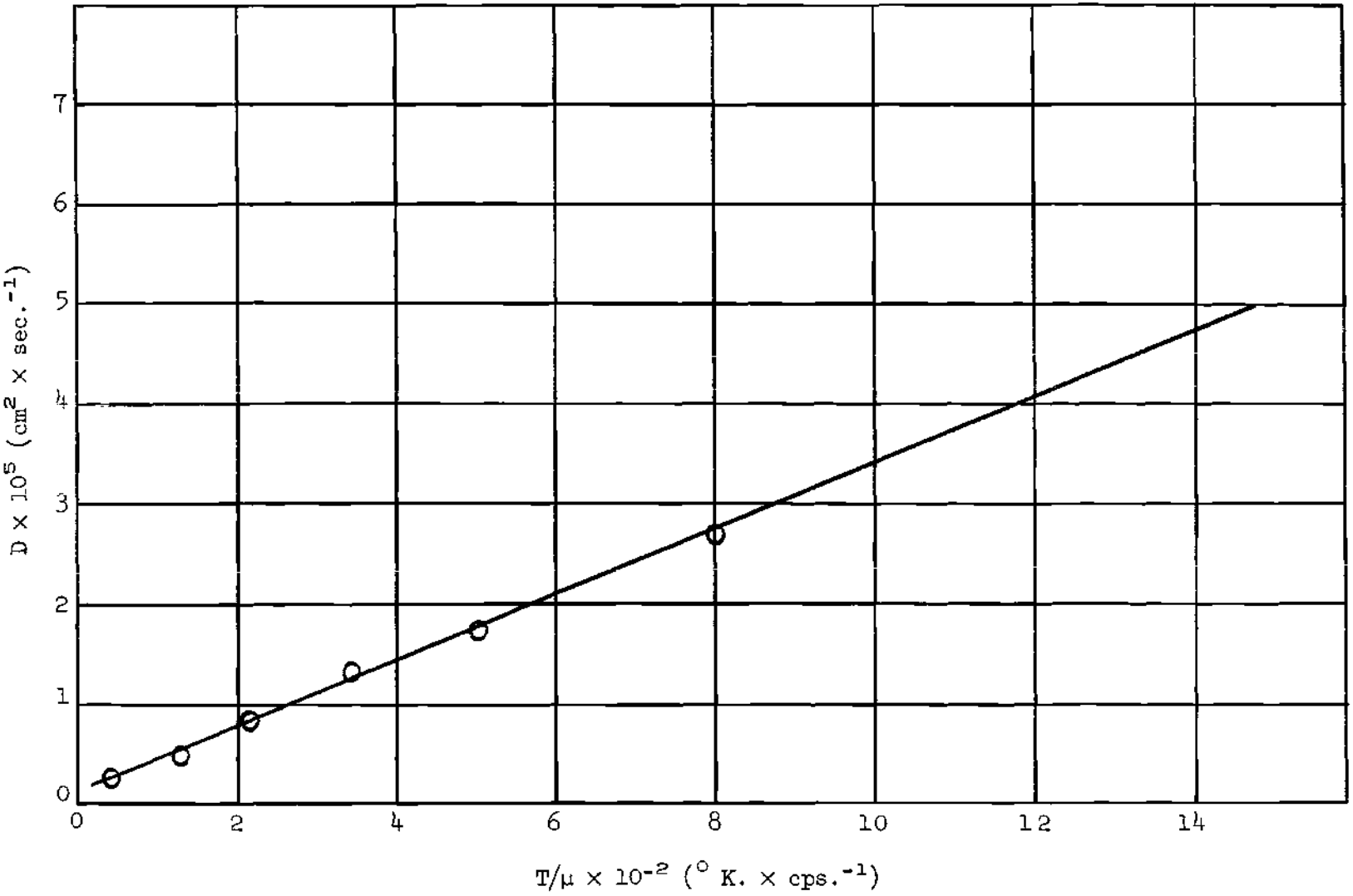

Figure 14. Diffusion of Water in Methanol

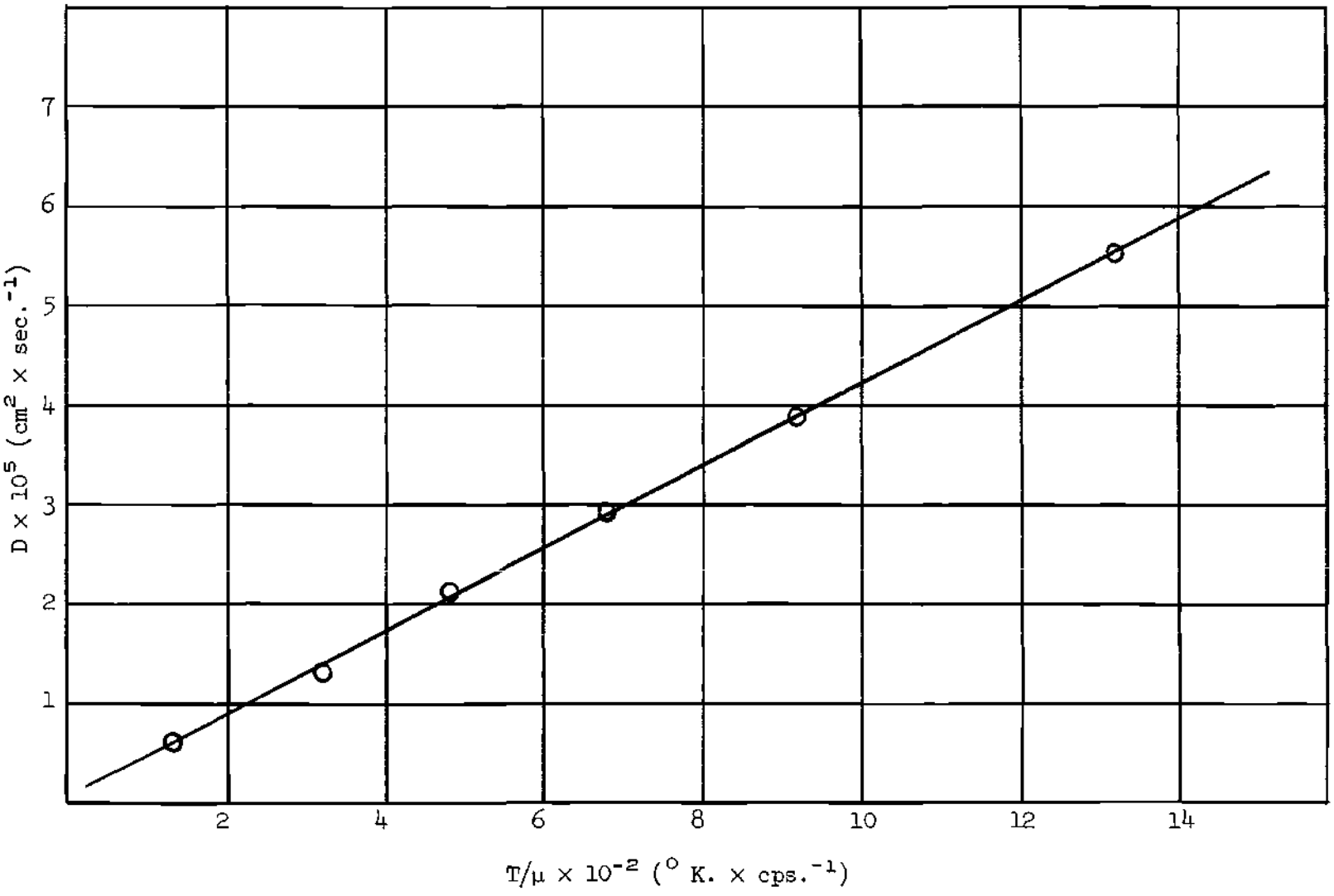

Figure 15. Diffusion of Water in ATN

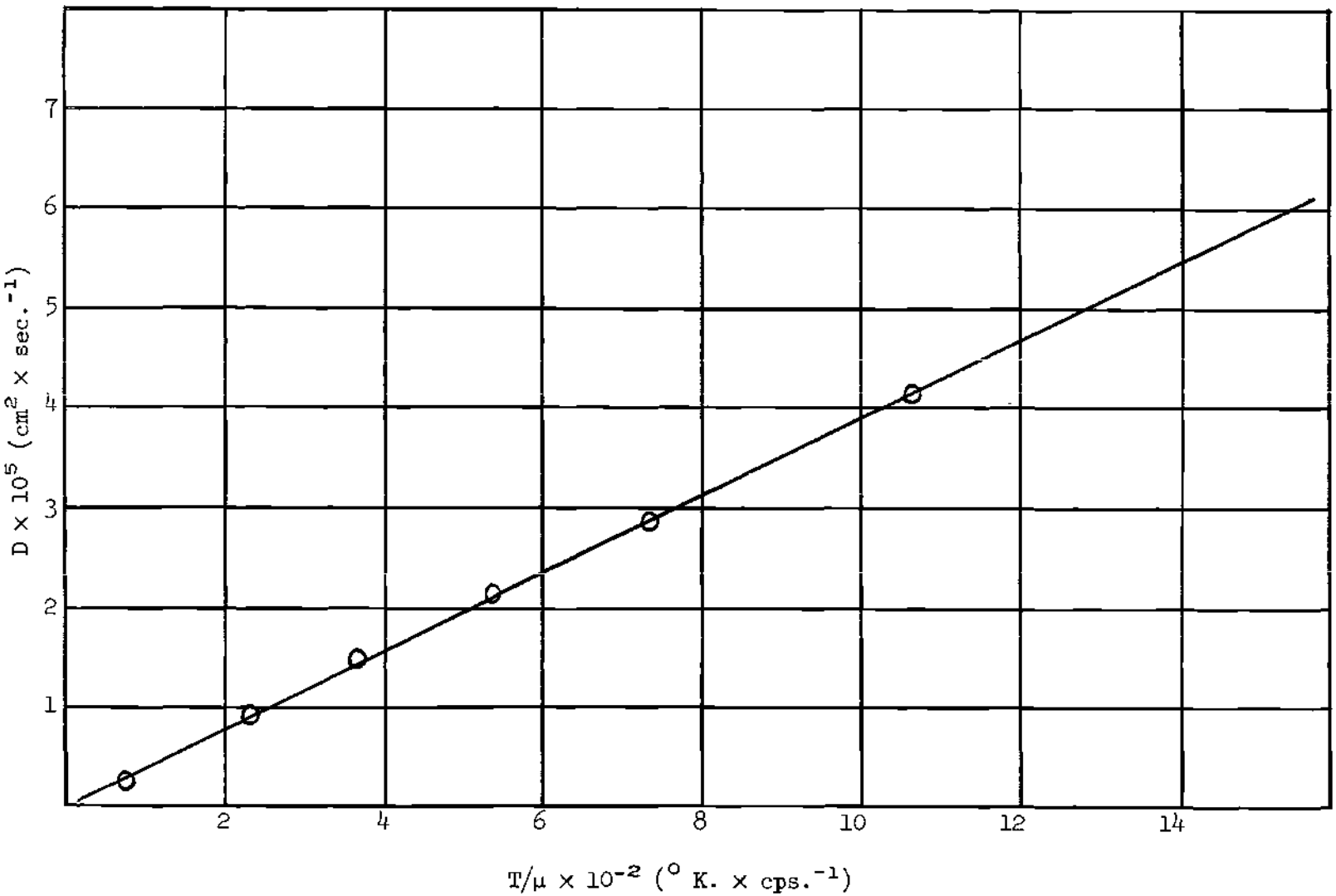

Figure 16. Diffusion of Water in MEK

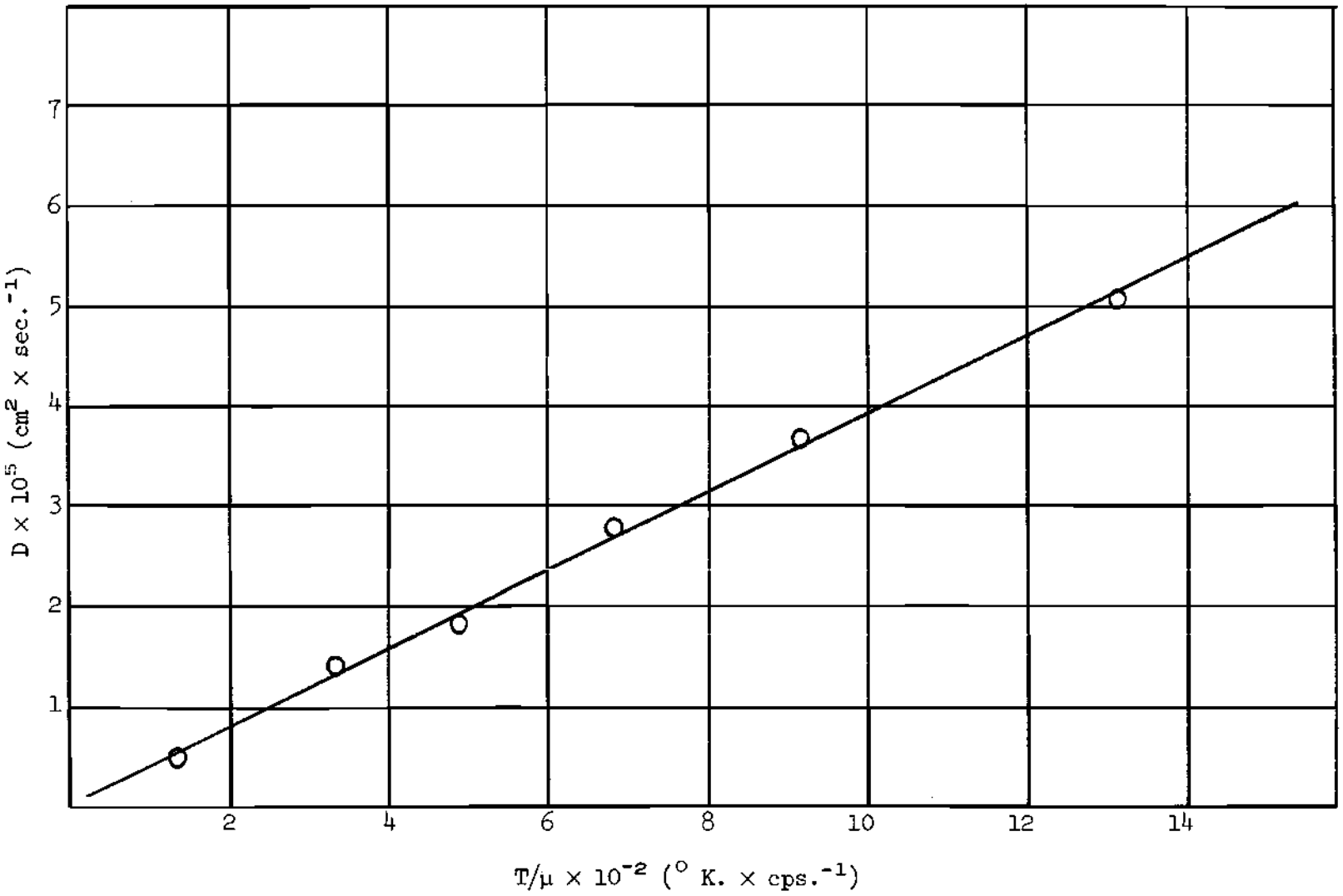

Figure 17. Diffusion of MeOH in ATN

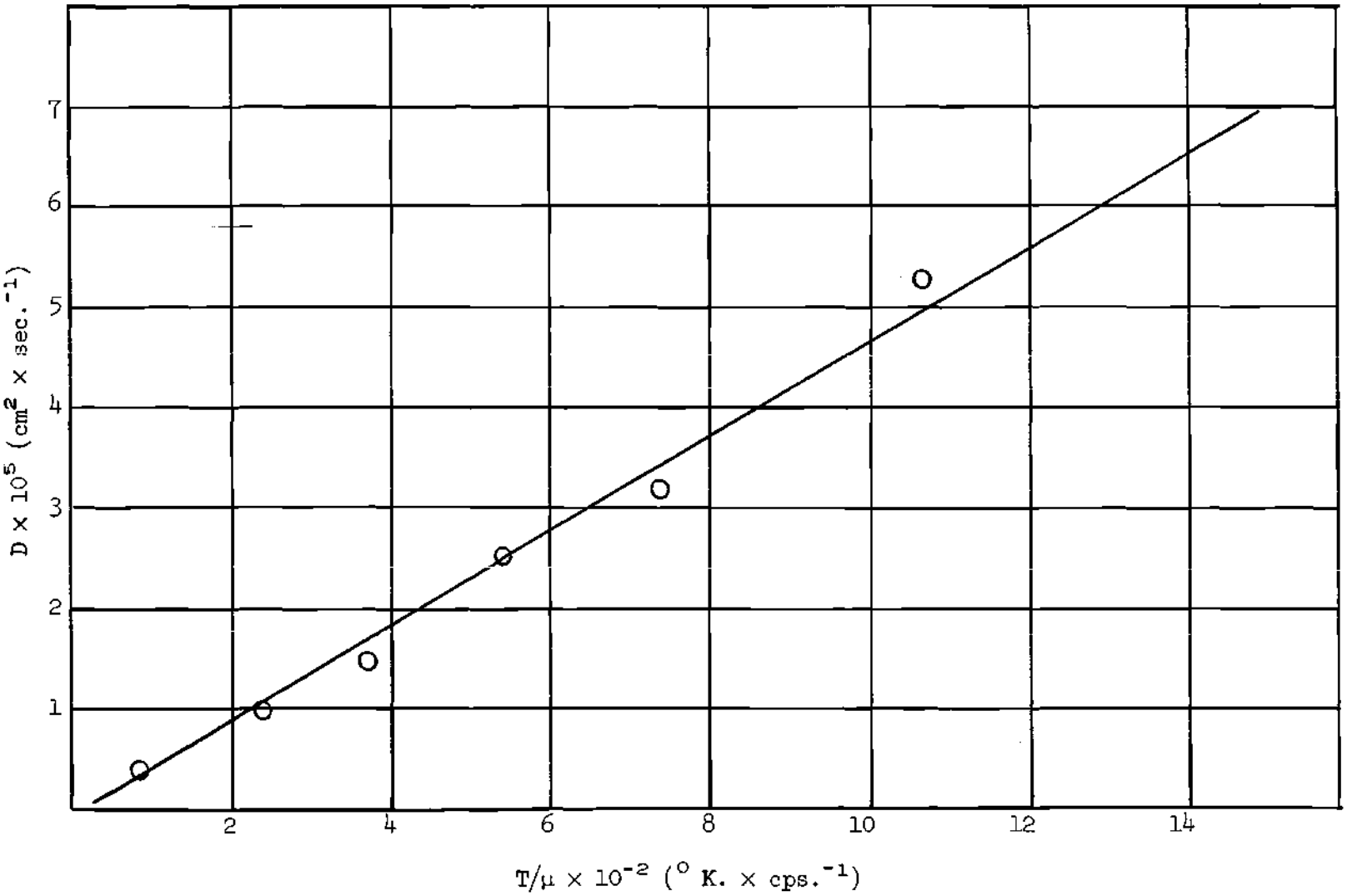

Figure 18. Diffusion of MeOH in MEK

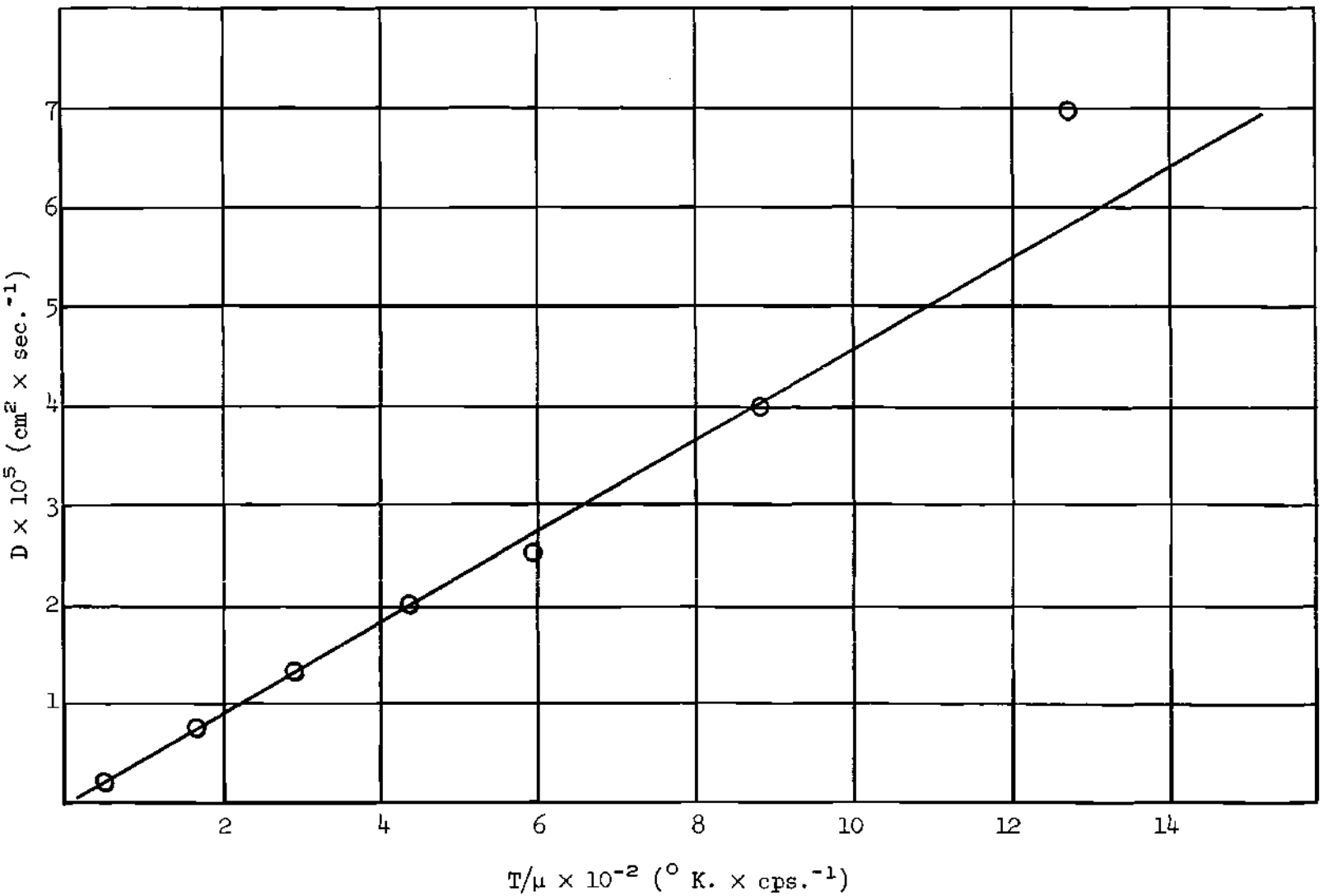

Figure 19. Diffusion of MeOH in MPK

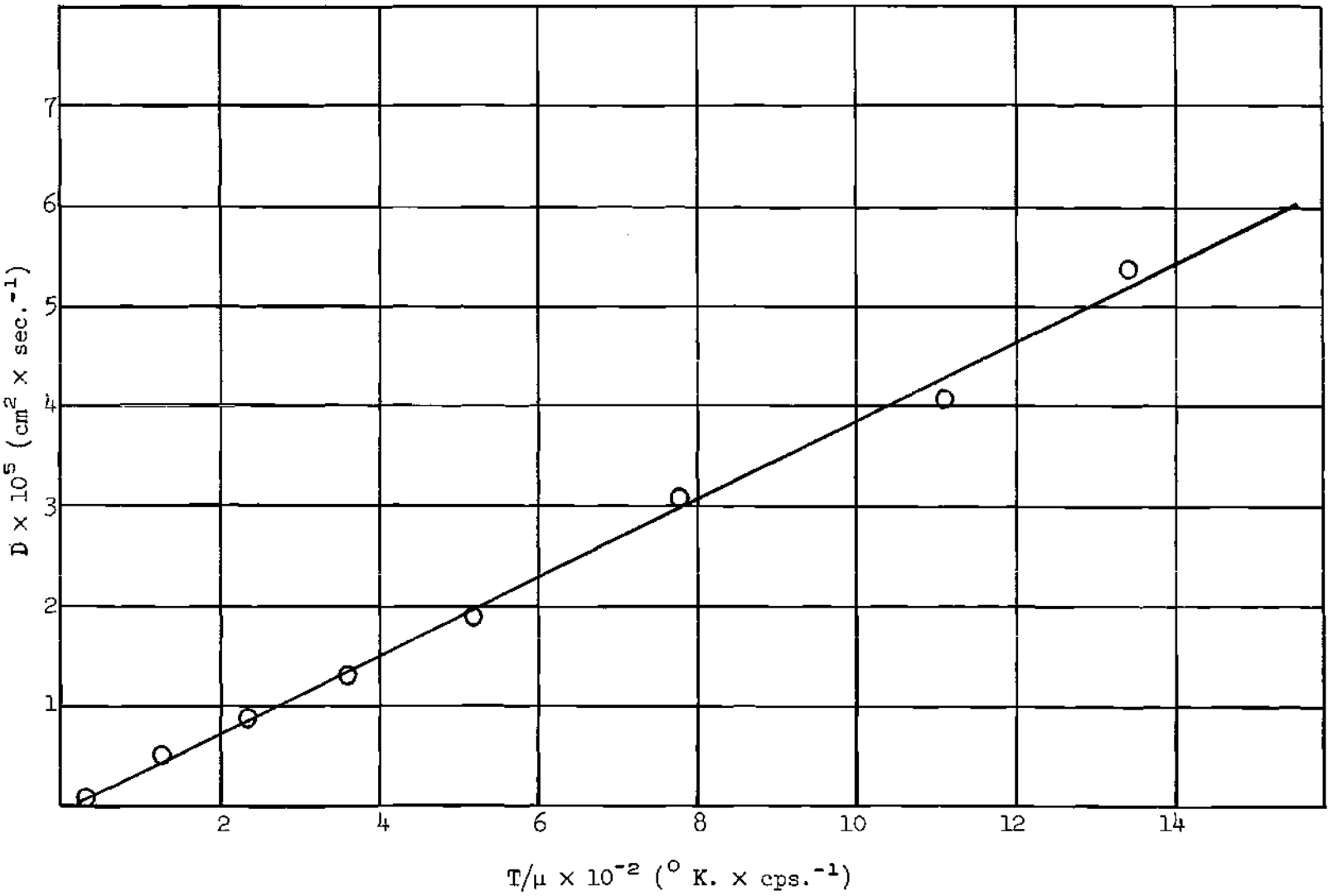

Figure 20. Diffusion of MeOH in MiBK

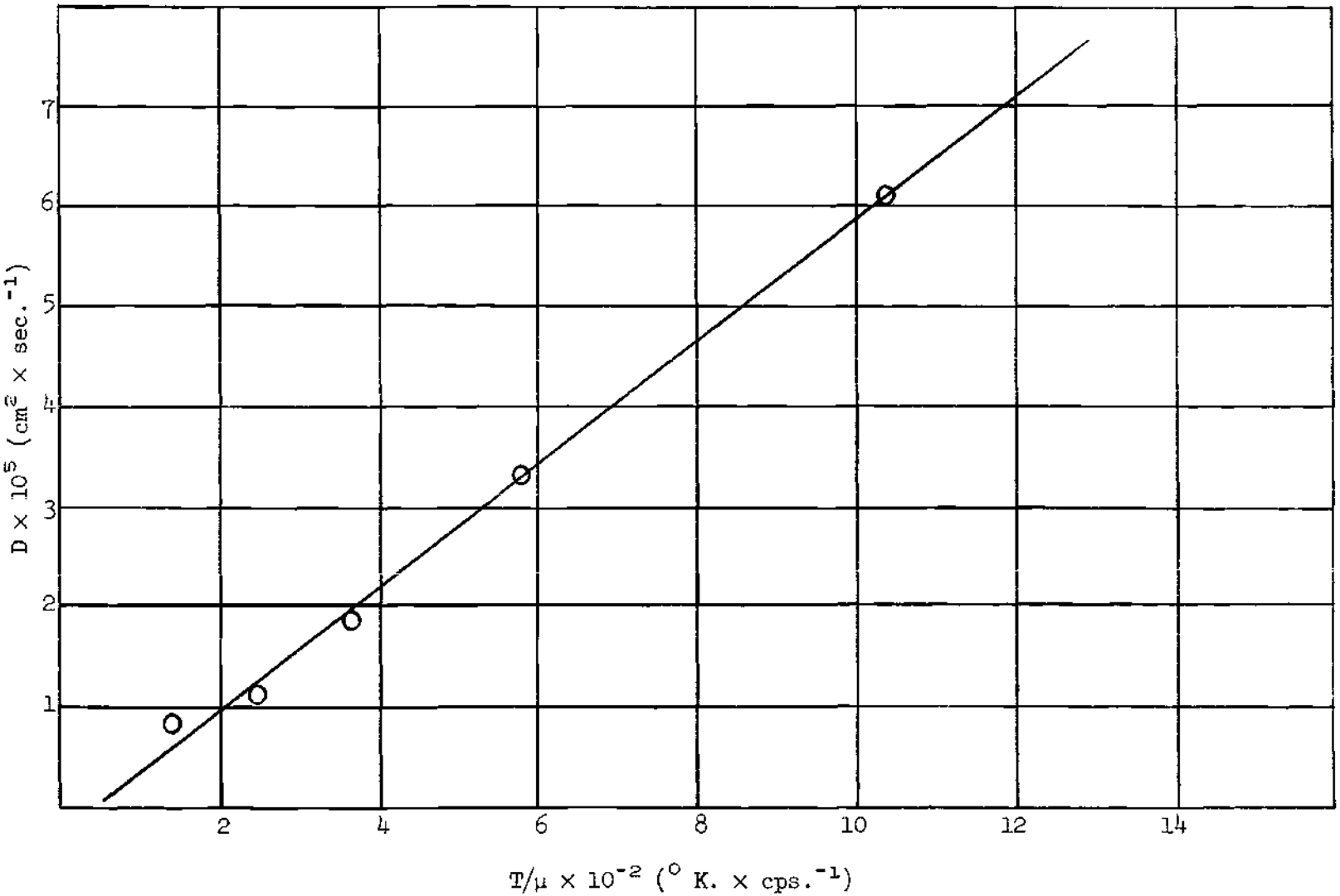

Figure 21. Diffusion of MeOH in MAK

CHAPTER VI

COMPARISON OF ESTIMATED VALUES OF D WITH EXPERIMENTAL VALUES AND DEVELOPMENT OF ESTIMATION METHODS FOR SELF-DIFFUSION AND BINARY DIFFUSION COEFFICIENTS

Since the results of this work strongly suggested that the factor $(T/\mu)^{1.0}$ was a good representation of the temperature function for the diffusion coefficient, those estimation methods for the diffusion coefficient which included this factor were compared with the experimental results. The reference substance method of Othmer and Thakar (Equation 1.37) was omitted since it contained the factor μ_w which was unknown at temperatures below 273° K. The equations of Li and Chang (Equation 1.24) and of Houghton (Equation 1.41) required some special considerations in order to apply them to diffusion in the binary systems studied.

The equation of Li and Chang was modified by using the molal volume of the solute and the viscosity of the solvent. In such dilute solutions as those used in this study, the solvent was essentially a continuous phase. The molal volume of the solute was used because the resulting equation,

$$D = \frac{kT}{2\pi\mu_v} \left(\frac{N}{V_u}\right)^{1/3} \tag{6.1}$$

gave the best agreement with the experimental values and was similar in

form to the Stokes-Einstein equation (Equation 1.7). The estimation method of Eyring (Equation 1.25) was identical to Equation 6.1 except for the factor 2π and was therefore not included in the comparison.

The estimation method of Houghton (Equation 1.41) was modified by using the atomic volume and molecular weight of the solute and the density and viscosity of the solvent for the binary system. The viscosity of the solvent was again an obvious system characteristic, but the other factors were assigned on the basis that the given combination gave the best agreement with the experimental values. The equation as used was

$$D = RT\ \rho_v (v_u)^{2/3}/6M_u\ \mu_v \qquad (6.2)$$

The equations of Wilke and Chang (Equation 1.29) and of Scheibel (Equation 1.39) were used as given. The association factor, ψ, was estimated to be 1.15 and the maximum ratio of (V_v/V_u) was set as equal to 0.500 for the ketones. For methanol, the recommended values of 1.9 and 0.666 were used respectively.

It was noted that the values for the association factors used by Wilke seemed to be related to the heat of vaporization of the solvent. Further examination revealed that the order of association parameters was the same as the order of the heats of vaporization per gram of solvent. The square roots of these specific heats of vaporization were compared as shown in Table 17. This comparison showed that when ψ is unknown, it can be estimated by the relation

Table 17. Estimation of Association Parameters for Use in Equation 1.29

Material	H/m	ξ	ξ/ξ_{MiBK}	ψ Wilke
H_2O	532	23.1	2.45	2.6
MeOH	264	16.3	1.73	1.9
EtOH	203	14.3	1.52	1.5
ATN	123	11.1	1.18	1.1
MEK	103	10.1	1.07	1.0
MPK	92.3	9.6	1.02	1.0
MiBK	86.1	9.4	1.0	1.0
MAK	83.0	9.1	.97	1.0
Benzene	93.8	9.68	1.03	1.0
Hexane	80.3	8.95	.95	1.0
Heptane	74.2	8.62	.92	1.0

$$\psi = \frac{1}{9.4} (H/M)^{1/2} \tag{6.3}$$

The minimum value for ψ is 1.0 for all systems.

Examination of data for self-diffusion which is included in Appendix V revealed that an unusually simple correlation existed in the various systems studied. This simple relationship was

$$\frac{D \mu_v}{T} = 4.0 \times 10^{-10} \tag{6.4}$$

The maximum deviation from this value among 22 of the 24 systems included in the table was approximately 22 percent. This indicates that the relation

$$\frac{D \mu}{T} = \frac{k}{2\pi} \left(\frac{N}{V}\right)^{1/3} \tag{6.5}$$

does not hold. The molal volume of n-$C_{32}H_{66}$ is approximately ten times that of ethanol, but the values of $D \mu/T$ for the two systems are 4.3×10^{-10} and 3.7×10^{-10} respectively.

Water and t-butyl alcohol show the maximum deviations from the proposed relationship. Water has an abnormally high value of 7.31×10^{-10} for $D \mu/T$ while the value for t-butyl alcohol is low, 2.8×10^{-10}. Water is often found not to fit such correlations and this deviation was not unexpected. The low value for t-butyl alcohol may be due to some sort of dimerization process, but enough information to explain this

deviation definitely is not available.

No such simple relationship existed among the values included in Appendix V for the group D μ/T in binary systems. However, several general correlations were noted. Each solute appeared to have a characteristic constant K_D, such that

$$\frac{D\,\mu_v}{T} = K_D \left(\frac{V_v}{V_u}\right)^{0.55} \tag{6.6}$$

Values of K_D ranged from 8.1×10^{-10} for water systems to 3.3×10^{-10} for diffusion in carbon tetrachloride, benzene and acetone.

If values for the diffusion coefficient of other solutes in a solvent are known, it is suggested that K_D be calculated from equation 6.6 for estimation purposes. Where no diffusion data are available, K_D may be approximated by the relation

$$K_D \times 10^{10} = 3.3\,\psi \tag{6.7}$$

so that the general equation becomes

$$\frac{D\,\mu_v}{T} \times 10^{10} = \left[0.350 \left(\frac{H_v}{M_v}\right)^{0.50}\right]\left(\frac{V_v}{V_u}\right)^{0.55} \tag{6.8}$$

with the following limiting conditions:

1. The minimum value for the group in brackets is 3.3.
2. The largest value for the ratio (V_v/V_u) is 2.5.

The agreement of equation 6.8 with the experimental values shown in Table 18 was better than that obtained by the other methods considered with the exception of equation 6.1. Each of the estimation methods predicted values for the diffusion of water that were higher than the experimental values. This might be explained by the fact that water becomes associated with the polar groupings on these solvent molecules. This would slow the diffusion rate by forming hydrogen bonds.

The diffusion coefficient of methanol was also estimated to be higher than the experimental values in all the systems studied except for the 2-heptanone system. For this system, the estimation methods gave values both higher and lower than the experimental values. The reason for this sudden change in behavior by addition of one methyl group may be associated with the beginning of non-ideality in the solution, but is not fully understood.

Table 26 in Appendix VII shows that equation 6.8 successfully predicts the value of the group $\frac{D\,\mu_v}{T}$ for a variety of systems.

TABLE 18. COMPARISON OF VALUES OF D CALCULATED BY SEVERAL METHODS WITH EXPERIMENTAL VALUES (SQ CM/SEC)X100,000

DIFFUSION OF WATER IN MEOH

T K.	EQN. 1.39	EQN. 6.1	EQN. 6.2	EQN. 1.29	EQN. 6.8	EXP. VAL.
195.0	.2894	.2227	.2518	.3726	.3150	.1370
233.0	.9443	.7269	.7892	1.2159	1.0510	.4950
253.0	1.6323	1.2566	1.3367	2.1018	1.8372	.8290
273.0	2.6086	2.0081	2.0931	3.3590	2.9691	1.3700
293.0	3.8657	2.9758	3.0378	4.9776	4.4505	1.7900
323.0	6.1666	4.7471	4.6868	7.9404	7.2312	2.7300

DIFFUSION OF WATER IN ATN

T K.	EQN. 1.39	EQN. 6.1	EQN. 6.2	EQN. 1.29	EQN. 6.8	EXP. VAL.
195.0	.9377	.7716	.8861	1.3520	.8351	.6200
233.0	2.3218	1.9106	2.0969	3.3475	2.0677	1.3400
253.0	3.4802	2.8639	3.0685	5.0177	3.0994	2.1500
273.0	4.9298	4.0567	4.2407	7.1077	4.3903	2.9800
293.0	6.6318	5.4573	5.5603	9.5615	5.9061	3.8700
323.0	9.5329	7.8446	7.6695	13.7443	8.4898	5.5800

DIFFUSION OF WATER IN MEK

T K.	EQN. 1.39	EQN. 6.1	EQN. 6.2	EQN. 1.29	EQN. 6.8	EXP. VAL.
195.0	.5503	.4529	.5245	.8841	.4444	.2600
233.0	1.6698	1.3740	1.5275	2.6823	1.3484	.9770
253.0	2.6461	2.1774	2.3665	4.2506	2.1368	1.4700
273.0	3.8777	3.1909	3.3890	6.2290	3.1314	2.1500
293.0	5.3154	4.3740	4.5393	8.5385	4.2924	2.8900
323.0	7.7104	6.3449	6.3635	12.3860	6.2266	4.1600

TABLE 18. COMPARISON OF VALUES OF D CALCULATED BY SEVERAL METHODS WITH EXPERIMENTAL VALUES (CONT.)

DIFFUSION OF MEOH IN ATN

T K.	EQN. 1.39	EQN. 6.1	EQN. 6.2	EQN. 1.29	EQN. 6.8	EXP. VAL.
195.0	.7152	.6111	.7975	.8261	.6937	.5210
233.0	1.7707	1.4930	1.9388	2.0454	1.7223	1.4500
253.0	2.6543	2.2230	2.8758	3.0660	2.5869	1.8600
273.0	3.7598	3.1279	4.0287	4.3431	3.6730	2.8300
293.0	5.0579	4.1789	5.3561	5.8425	4.9542	3.7200
323.0	7.2705	5.9412	7.5540	8.3983	7.1524	5.1000
353.0	9.6586	7.7946	9.8270	11.1568	9.5452	.0000
368.0	10.8721	8.7122	10.9371	12.5586	10.7692	.0000

DIFFUSION OF MEOH IN MEK

T K.	EQN. 1.39	EQN. 6.1	EQN. 6.2	EQN. 1.29	EQN. 6.8	EXP. VAL.
195.0	.4197	.3586	.4721	.5402	.4139	.4090
233.0	1.2735	1.0738	1.4123	1.6390	1.2561	1.0000
253.0	2.0181	1.6902	2.2179	2.5973	1.9930	1.5200
273.0	2.9574	2.4603	3.2196	3.8062	2.9250	2.5700
293.0	4.0539	3.3494	4.3726	5.2174	4.0145	3.2000
323.0	5.8805	4.8053	6.2677	7.5683	5.8259	5.3200
353.0	7.7689	6.2696	8.2203	9.9987	7.6741	.0000
368.0	8.6899	6.9636	9.1858	11.1840	8.5548	.0000

TABLE 18. COMPARISON OF VALUES OF D CALCULATED BY SEVERAL METHODS WITH EXPERIMENTAL VALUES (CONT.)

DIFFUSION OF MEOH IN MPK

T K.	EQN. 1.39	EQN. 6.1	EQN. 6.2	EQN. 1.29	EQN. 6.8	EXP. VAL.
195.0	.2723	.2327	.3046	.3831	.2748	.2270
233.0	.8937	.7536	.9867	1.2572	.9021	.7810
253.0	1.5712	1.3159	1.7232	2.2102	1.5859	1.3800
273.0	2.3919	1.9898	2.6051	3.3646	2.4143	2.0100
293.0	3.2886	2.7171	3.5549	4.6260	3.3194	2.5300
323.0	4.8384	3.9537	5.1651	6.8060	4.8837	4.0200
353.0	7.0140	5.6603	7.3862	9.8663	7.0796	6.8000
368.0	8.5640	6.8626	8.9565	12.0467	8.6442	.0000

DIFFUSION OF MEOH IN MIBK

T K.	EQN. 1.39	EQN. 6.1	EQN. 6.2	EQN. 1.29	EQN. 6.8	EXP. VAL.
195.0	.1691	.1445	.1866	.2566	.1674	.1260
233.0	.6950	.5860	.7598	1.0544	.6878	.5590
253.0	1.2779	1.0703	1.3884	1.9385	1.2646	.9300
273.0	2.0169	1.6779	2.1774	3.0595	1.9959	1.3800
293.0	2.8527	2.3569	3.0605	4.3273	2.8230	1.9700
323.0	4.2900	3.5056	4.5597	6.5075	4.2452	3.0900
353.0	6.1640	4.9744	6.4796	9.3503	6.0998	4.0900
368.0	7.4020	5.9315	7.7242	11.2283	7.3248	5.4000

TABLE 18. COMPARISON OF VALUES OF D CALCULATED BY SEVERAL METHODS WITH EXPERIMENTAL VALUES (CONT.)

DIFFUSION OF MEOH IN MAK

T K.	EQN. 1.39	EQN. 6.1	EQN. 6.2	EQN. 1.29	EQN. 6.8	EXP. VAL.
195.0	.0030	.0026	.0034	.0050	.0029	.0000
233.0	.3398	.2865	.3763	.5507	.3262	.0000
253.0	.8003	.6703	.8827	1.2968	.7682	.8190
273.0	1.3567	1.1286	1.4891	2.1983	1.3022	1.1500
293.0	1.9980	1.6508	2.1815	3.2374	1.9179	1.9300
323.0	3.1941	2.6101	3.4584	5.1755	3.0660	3.3800
353.0	4.7666	3.8467	5.1213	7.7234	4.5754	.0000
368.0	5.7073	4.5735	6.1131	9.2477	5.4784	6.1800

CHAPTER VII

CONCLUSIONS

The following conclusions are drawn from the results of the investigation:

1. The temperature function for the diffusion coefficient in both self-diffusion and dilute binary diffusion systems is well represented by the relation

$$D = K_{system} (T/\mu)^{1.0} \tag{7.1}$$

where the constant may include contributions from the solvent and the solute.

2. The constant, K_{system}, for self-diffusion in 22 liquids with a molal volume ratio of 10:1 is approximately constant with a value of 4×10^{-10}.

3. The theoretically derived relation for self-diffusion in liquids

$$\frac{D\mu}{T} = K_{system} \left(\frac{N}{V}\right)^{1/3} \tag{7.2}$$

is not compatible with the fact that although the molal volume of liquids for which the self-diffusion data are available vary by a factor of ten,

the value of the right side of equation 7.2 remains approximately constant at a value of 4.0×10^{-10}.

4. In self-diffusion systems, the diffusion rate of water is unusually high compared with the rate which would be expected from consideration of other materials.

5. In dilute binary solutions, each solvent seems to have an associated constant, K_D, such that

$$\frac{D\,\mu_V}{T} = K_D \left(\frac{V_v}{V_u}\right)^{0.55} \tag{7.3}$$

6. The increased diffusion coefficients in "associated" solvents relative to normal liquids with the same value of (T/μ) is approximately proportional to the value of the ratio

$$\left[(H/M)_A/(H/M)_{MiBK}\right]^{0.50}$$

7. The diffusion coefficient in dilute binary solutions may be estimated by the relation

$$\frac{D\,\mu}{T} \times 10^{10} = \left[0.350 \left(\frac{H_v}{M_v}\right)^{0.50}\right] \left(\frac{V_v}{V_u}\right)^{0.55} \tag{7.4}$$

with the following limiting conditions:

a. The minimum value of the bracketed factor is 3.3.

b. The maximum value of the ratio (V_v/V_u) is 2.5.

APPENDICES

APPENDIX I

EMF OF IRON-ADVANCE THERMOCOUPLES RELATIVE TO 273° K. JUNCTION

TABLE 19. EMF OF IRON-ADVANCE THERMOCOUPLES RELATIVE TO 273 K. JUNCTION (MILLIVOLTS)

T	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0
190	-2.7693	-2.7392	-2.7089	-2.6786	-2.6483	-2.6178	-2.5873	-2.5566	-2.5259	-2.4952
200	-2.4643	-2.4334	-2.4024	-2.3713	-2.3401	-2.3089	-2.2775	-2.2461	-2.2147	-2.1831
210	-2.1515	-2.1197	-2.0879	-2.0561	-2.0241	-1.9921	-1.9600	-1.9278	-1.8955	-1.8632
220	-1.8307	-1.7982	-1.7657	-1.7330	-1.7003	-1.6674	-1.6346	-1.6016	-1.5685	-1.5354
230	-1.5022	-1.4689	-1.4355	-1.4021	-1.3686	-1.3350	-1.3013	-1.2675	-1.2337	-1.1998
240	-1.1658	-1.1317	-1.0976	-1.0633	-1.0290	-.9946	-.9602	-.9256	-.8910	-.8563
250	-.8215	-.7867	-.7517	-.7167	-.6816	-.6464	-.6112	-.5759	-.5405	-.5050
260	-.4694	-.4338	-.3980	-.3622	-.3264	-.2904	-.2544	-.2183	-.1821	-.1458
270	-.1095	-.0730	-.0365	.0000	.0366	.0734	.1102	.1471	.1841	.2211
280	.2583	.2955	.3328	.3701	.4076	.4451	.4827	.5204	.5582	.5960
290	.6339	.6719	.7100	.7481	.7864	.8247	.8631	.9015	.9401	.9787
300	1.0174	1.0562	1.0951	1.1340	1.1730	1.2121	1.2513	1.2906	1.3299	1.3693
310	1.4088	1.4484	1.4880	1.5277	1.5675	1.6074	1.6474	1.6874	1.7275	1.7677
320	1.8080	1.8483	1.8888	1.9293	1.9699	2.0105	2.0513	2.0921	2.1330	2.1740
330	2.2151	2.2562	2.2974	2.3387	2.3801	2.4215	2.4631	2.5047	2.5464	2.5881
340	2.6300	2.6719	2.7139	2.7560	2.7981	2.8404	2.8827	2.9251	2.9675	3.0101
350	3.0527	3.0954	3.1382	3.1811	3.2240	3.2670	3.3101	3.3533	3.3966	3.4399
360	3.4833	3.5268	3.5704	3.6140	3.6578	3.7016	3.7455	3.7894	3.8335	3.8776
370	3.9218	3.9661	4.0104	4.0549	4.0994	4.1440	4.1886	4.2334	4.2782	4.3231
380	4.3681	4.4132	4.4583	4.5035	4.5488	4.5942	4.6397	4.6852	4.7308	4.7765

APPENDIX II

CALIBRATION OF GAS THERMO-REGULATOR

TABLE 20. CALIBRATION OF GAS THERMO-REGULATOR (MM HG/ K)

T1	T2	P1	P2	DP/DT
190	191	740.00	743.70	3.70
200	201	740.00	743.51	3.51
210	211	740.00	743.34	3.34
220	221	740.00	743.19	3.19
230	231	740.00	743.05	3.05
240	241	740.00	742.93	2.93
250	251	740.00	742.81	2.81
260	261	740.00	742.70	2.70
270	271	740.00	742.60	2.60
280	281	740.00	742.51	2.51

APPENDIX III

DENSITY DATA FOR SYSTEMS STUDIED

TABLE 21. DENSITY DATA FOR SYSTEMS STUDIED (GM/CC)

T	MOH-H2O	ATN-H2O	MEK-H2O	ATN-MOH	MEK-MOH	MPK-MOH	MIBK-MOH	MAK-MOH
190	.8823	.8967	.9036	.8969	.9031	.0000	.8854	.0000
191	.8813	.8956	.9027	.8957	.9021	.0000	.8847	.0000
192	.8803	.8946	.9018	.8946	.9012	.0000	.8839	.0000
193	.8794	.8935	.9008	.8934	.9003	.0000	.8831	.0000
194	.8784	.8924	.8999	.8923	.8994	.0000	.8823	.0000
195	.8774	.8913	.8990	.8912	.8985	.0000	.8816	.0000
196	.8764	.8903	.8980	.8900	.8975	.8930	.8808	.0000
197	.8755	.8892	.8971	.8889	.8966	.8920	.8800	.0000
198	.8745	.8881	.8962	.8878	.8957	.8910	.8792	.0000
199	.8735	.8871	.8952	.8867	.8948	.8900	.8784	.0000
200	.8726	.8860	.8943	.8856	.8938	.8890	.8776	.0000
201	.8716	.8850	.8934	.8844	.8929	.8881	.8768	.0000
202	.8707	.8839	.8924	.8833	.8920	.8871	.8760	.0000
203	.8697	.8829	.8915	.8822	.8910	.8862	.8752	.0000
204	.8688	.8818	.8906	.8812	.8901	.8852	.8744	.0000
205	.8678	.8807	.8896	.8801	.8892	.8843	.8736	.0000
206	.8669	.8797	.8887	.8790	.8882	.8833	.8728	.0000
207	.8659	.8786	.8877	.8779	.8873	.8824	.8720	.0000
208	.8650	.8776	.8868	.8768	.8863	.8814	.8712	.0000
209	.8641	.8766	.8858	.8758	.8854	.8805	.8704	.0000
210	.8632	.8755	.8849	.8747	.8845	.8796	.8696	.0000
211	.8622	.8745	.8839	.8736	.8835	.8786	.8687	.0000
212	.8613	.8734	.8830	.8726	.8826	.8777	.8679	.0000
213	.8604	.8724	.8820	.8715	.8816	.8768	.8671	.0000
214	.8595	.8714	.8811	.8704	.8807	.8759	.8663	.0000
215	.8586	.8703	.8801	.8694	.8797	.8750	.8655	.0000
216	.8577	.8693	.8792	.8683	.8788	.8741	.8646	.0000
217	.8568	.8683	.8782	.8673	.8778	.8732	.8638	.0000
218	.8559	.8672	.8773	.8663	.8769	.8723	.8630	.0000
219	.8550	.8662	.8763	.8652	.8759	.8714	.8622	.0000

TABLE 21. DENSITY DATA CONTINUED

T	MOH-H2O	ATN-H2O	MEK-H2O	ATN-MOH	MEK-MOH	MPK-MOH	MIBK-MOH	MAK-MOH
220	.8541	.8652	.8754	.8642	.8750	.8705	.8613	.0000
221	.8532	.8641	.8744	.8632	.8740	.8696	.8605	.0000
222	.8523	.8631	.8734	.8621	.8731	.8687	.8597	.0000
223	.8514	.8621	.8725	.8611	.8721	.8678	.8588	.0000
224	.8505	.8611	.8715	.8601	.8712	.8669	.8580	.0000
225	.8496	.8600	.8706	.8590	.8702	.8660	.8572	.0000
226	.8487	.8590	.8696	.8580	.8692	.8651	.8563	.0000
227	.8479	.8580	.8686	.8570	.8683	.8642	.8555	.0000
228	.8470	.8570	.8677	.8560	.8673	.8634	.8547	.0000
229	.8461	.8559	.8667	.8550	.8664	.8625	.8539	.0000
230	.8452	.8549	.8658	.8540	.8654	.8616	.8530	.0000
231	.8444	.8539	.8648	.8530	.8644	.8607	.8522	.0000
232	.8435	.8529	.8638	.8520	.8635	.8599	.8514	.0000
233	.8426	.8519	.8629	.8510	.8625	.8590	.8505	.0000
234	.8418	.8508	.8619	.8500	.8616	.8581	.8497	.0000
235	.8409	.8498	.8609	.8490	.8606	.8573	.8489	.0000
236	.8401	.8488	.8600	.8480	.8596	.8564	.8480	.0000
237	.8392	.8478	.8590	.8470	.8587	.8555	.8472	.0000
238	.8383	.8468	.8580	.8460	.8577	.8547	.8464	.0000
239	.8375	.8458	.8571	.8450	.8568	.8538	.8455	.0000
240	.8366	.8448	.8561	.8440	.8558	.8529	.8447	.0000
241	.8358	.8437	.8551	.8430	.8548	.8521	.8439	.0000
242	.8349	.8427	.8542	.8420	.8539	.8512	.8430	.0000
243	.8341	.8417	.8532	.8410	.8529	.8504	.8422	.0000
244	.8332	.8407	.8522	.8400	.8519	.8495	.8414	.0000
245	.8324	.8397	.8513	.8390	.8510	.8487	.8405	.0000
246	.8315	.8387	.8503	.8381	.8500	.8478	.8397	.8518
247	.8307	.8377	.8493	.8371	.8490	.8469	.8389	.8511
248	.8298	.8367	.8484	.8361	.8481	.8461	.8380	.8503
249	.8290	.8357	.8474	.8351	.8471	.8452	.8372	.8495

TABLE 21. DENSITY DATA CONTINUED

T	MOH-H2O	ATN-H2O	MEK-H2O	ATN-MOH	MEK-MOH	MPK-MOH	MIBK-MOH	MAK-MOH
250	.8282	.8346	.8464	.8341	.8462	.8444	.8364	.8488
251	.8273	.8336	.8455	.8331	.8452	.8435	.8356	.8480
252	.8265	.8326	.8445	.8322	.8442	.8427	.8347	.8473
253	.8256	.8316	.8436	.8312	.8433	.8418	.8339	.8465
254	.8248	.8306	.8426	.8302	.8423	.8410	.8331	.8458
255	.8240	.8296	.8416	.8292	.8413	.8401	.8322	.8450
256	.8231	.8286	.8407	.8282	.8404	.8393	.8314	.8442
257	.8223	.8276	.8397	.8273	.8394	.8384	.8306	.8435
258	.8215	.8266	.8387	.8263	.8385	.8376	.8298	.8427
259	.8206	.8256	.8378	.8253	.8375	.8367	.8289	.8419
260	.8198	.8245	.8368	.8243	.8365	.8359	.8281	.8412
261	.8190	.8235	.8358	.8233	.8356	.8350	.8273	.8404
262	.8181	.8225	.8349	.8224	.8346	.8341	.8265	.8397
263	.8173	.8215	.8339	.8214	.8337	.8333	.8257	.8389
264	.8165	.8205	.8330	.8204	.8327	.8324	.8248	.8381
265	.8157	.8195	.8320	.8194	.8317	.8316	.8240	.8373
266	.8148	.8185	.8310	.8184	.8308	.8307	.8232	.8366
267	.8140	.8175	.8301	.8174	.8298	.8299	.8224	.8358
268	.8132	.8164	.8291	.8164	.8289	.8290	.8216	.8350
269	.8123	.8154	.8282	.8155	.8279	.8282	.8207	.8343
270	.8115	.8144	.8272	.8145	.8270	.8273	.8199	.8335
271	.8107	.8134	.8263	.8135	.8260	.8264	.8191	.8327
272	.8098	.8124	.8253	.8125	.8251	.8256	.8183	.8319
273	.8090	.8114	.8244	.8115	.8241	.8247	.8175	.8312
274	.8082	.8103	.8234	.8105	.8232	.8239	.8167	.8304
275	.8074	.8093	.8224	.8095	.8222	.8230	.8158	.8296
276	.8065	.8083	.8215	.8085	.8213	.8221	.8150	.8288
277	.8057	.8073	.8205	.8075	.8203	.8213	.8142	.8280
278	.8049	.8063	.8196	.8065	.8194	.8204	.8134	.8272
279	.8040	.8052	.8186	.8055	.8184	.8195	.8126	.8265

TABLE 21. DENSITY DATA CONTINUED

T	MOH-H2O	ATN-H2O	MEK-H2O	ATN-MOH	MEK-MOH	MPK-MOH	MIBK-MOH	MAK-MOH
280	.8032	.8042	.8177	.8045	.8175	.8187	.8118	.8257
281	.8024	.8032	.8168	.8035	.8165	.8178	.8110	.8249
282	.8015	.8022	.8158	.8025	.8156	.8169	.8101	.8241
283	.8007	.8011	.8149	.8015	.8146	.8161	.8093	.8233
284	.7999	.8001	.8139	.8005	.8137	.8152	.8085	.8225
285	.7990	.7991	.8130	.7995	.8128	.8143	.8077	.8217
286	.7982	.7981	.8120	.7984	.8118	.8134	.8069	.8209
287	.7974	.7970	.8111	.7974	.8109	.8126	.8061	.8201
288	.7965	.7960	.8102	.7964	.8100	.8117	.8053	.8193
289	.7957	.7950	.8092	.7954	.8090	.8108	.8044	.8186
290	.7949	.7939	.8083	.7943	.8081	.8099	.8036	.8178
291	.7940	.7929	.8074	.7933	.8072	.8090	.8028	.8170
292	.7932	.7919	.8064	.7923	.8062	.8081	.8020	.8162
293	.7923	.7908	.8055	.7912	.8053	.8072	.8012	.8154
294	.7915	.7898	.8046	.7902	.8044	.8064	.8004	.8146
295	.7906	.7887	.8036	.7892	.8035	.8055	.7996	.8138
296	.7898	.7877	.8027	.7881	.8025	.8046	.7987	.8129
297	.7890	.7866	.8018	.7871	.8016	.8037	.7979	.8121
298	.7881	.7856	.8009	.7860	.8007	.8028	.7971	.8113
299	.7873	.7846	.8000	.7850	.7998	.8019	.7963	.8105
300	.7864	.7835	.7990	.7839	.7989	.8010	.7955	.8097
301	.7856	.7825	.7981	.7828	.7980	.8001	.7947	.8089
302	.7847	.7814	.7972	.7818	.7970	.7992	.7938	.8081
303	.7838	.7803	.7963	.7807	.7961	.7983	.7930	.8073
304	.7830	.7793	.7954	.7796	.7952	.7974	.7922	.8065
305	.7821	.7782	.7945	.7786	.7943	.7964	.7914	.8057
306	.7813	.7772	.7936	.7775	.7934	.7955	.7906	.8048
307	.7804	.7761	.7927	.7764	.7925	.7946	.7897	.8040
308	.7795	.7750	.7917	.7753	.7916	.7937	.7889	.8032
309	.7787	.7740	.7908	.7742	.7907	.7928	.7881	.8024

TABLE 21. DENSITY DATA CONTINUED

T	MOH-H2O	ATN-H2O	MEK-H2O	ATN-MOH	MEK-MOH	MPK-MOH	MIBK-MOH	MAK-MOH
310	.7778	.7729	.7899	.7731	.7898	.7919	.7872	.8016
311	.7769	.7718	.7890	.7720	.7889	.7909	.7864	.8007
312	.7761	.7708	.7881	.7709	.7880	.7900	.7856	.7999
313	.7752	.7697	.7873	.7698	.7871	.7891	.7847	.7991
314	.7743	.7686	.7864	.7687	.7863	.7881	.7839	.7983
315	.7734	.7675	.7855	.7675	.7854	.7872	.7831	.7974
316	.7725	.7665	.7846	.7664	.7845	.7863	.7822	.7966
317	.7717	.7654	.7837	.7653	.7836	.7853	.7814	.7958
318	.7708	.7643	.7828	.7641	.7827	.7844	.7805	.7949
319	.7699	.7632	.7819	.7630	.7819	.7835	.7797	.7941
320	.7690	.7621	.7811	.7619	.7810	.7825	.7788	.7933
321	.7681	.7610	.7802	.7607	.7801	.7816	.7780	.7924
322	.7672	.7599	.7793	.7595	.7792	.7806	.7771	.7916
323	.7663	.7588	.7784	.7584	.7784	.7797	.7763	.7908
324	.7654	.7577	.7776	.7572	.7775	.7787	.7754	.7899
325	.7645	.7566	.7767	.7560	.7767	.7778	.7745	.7891
326	.7636	.7555	.7758	.7549	.7758	.7768	.7737	.7883
327	.7627	.7544	.7750	.7537	.7749	.7758	.7728	.7874
328	.7618	.7533	.7741	.7525	.7741	.7749	.7719	.7866
329	.7608	.7522	.7733	.7513	.7732	.7739	.7711	.7857
330	.7599	.0000	.7724	.0000	.7724	.7729	.7702	.7849
331	.7590	.0000	.7715	.0000	.7715	.7720	.7693	.7840
332	.7581	.0000	.7707	.0000	.7707	.7710	.7684	.7832
333	.7571	.0000	.7698	.0000	.7699	.7700	.7675	.7823
334	.7562	.0000	.7690	.0000	.7690	.7690	.7666	.7815
335	.7553	.0000	.7682	.0000	.7682	.7680	.7657	.7806
336	.7543	.0000	.7673	.0000	.7674	.7671	.7648	.7798
337	.7534	.0000	.7665	.0000	.7665	.7661	.7639	.7789
338	.0000	.0000	.7657	.0000	.7657	.7651	.7630	.7781
339	.0000	.0000	.7648	.0000	.7649	.7641	.7621	.7772

TABLE 21. DENSITY DATA CONTINUED

T	MOH-H2O	ATN-H2O	MEK-H2O	ATN-MOH	MEK-MOH	MPK-MOH	MIBK-MOH	MAK-MOH
340	.0000	.0000	.7640	.0000	.7641	.7631	.7611	.7764
341	.0000	.0000	.7632	.0000	.7633	.7621	.7602	.7755
342	.0000	.0000	.7624	.0000	.7624	.7611	.7593	.7747
343	.0000	.0000	.7615	.0000	.7616	.7601	.7583	.7738
344	.0000	.0000	.7607	.0000	.7608	.7591	.7574	.7729
345	.0000	.0000	.7599	.0000	.7600	.7581	.7564	.7721
346	.0000	.0000	.7591	.0000	.7592	.7571	.7555	.7712
347	.0000	.0000	.7583	.0000	.7584	.7561	.7545	.7703
348	.0000	.0000	.7575	.0000	.7576	.7551	.7536	.7695
349	.0000	.0000	.7567	.0000	.7568	.7540	.7526	.7686
350	.0000	.0000	.7559	.0000	.7561	.7530	.7516	.7678
351	.0000	.0000	.7551	.0000	.7553	.7520	.7506	.7669
352	.0000	.0000	.7543	.0000	.7545	.7510	.7496	.7660
353	.0000	.0000	.0000	.0000	.0000	.7499	.7486	.7651
354	.0000	.0000	.0000	.0000	.0000	.7489	.7476	.7643
355	.0000	.0000	.0000	.0000	.0000	.7479	.7466	.7634
356	.0000	.0000	.0000	.0000	.0000	.7469	.7456	.7625
357	.0000	.0000	.0000	.0000	.0000	.7458	.7445	.7617
358	.0000	.0000	.0000	.0000	.0000	.7448	.7435	.7608
359	.0000	.0000	.0000	.0000	.0000	.7437	.7424	.7599
360	.0000	.0000	.0000	.0000	.0000	.7427	.7414	.7590
361	.0000	.0000	.0000	.0000	.0000	.7417	.7403	.7582
362	.0000	.0000	.0000	.0000	.0000	.7406	.7393	.7573
363	.0000	.0000	.0000	.0000	.0000	.7396	.7382	.7564
364	.0000	.0000	.0000	.0000	.0000	.7385	.7371	.7555
365	.0000	.0000	.0000	.0000	.0000	.7374	.7360	.7547
366	.0000	.0000	.0000	.0000	.0000	.7364	.7349	.7538
367	.0000	.0000	.0000	.0000	.0000	.7353	.7338	.7529
368	.0000	.0000	.0000	.0000	.0000	.7343	.7326	.7520
369	.0000	.0000	.0000	.0000	.0000	.7332	.7315	.7511

TABLE 21. DENSITY DATA CONTINUED

T	MOH-H2O	ATN-H2O	MEK-H2O	ATN-MOH	MEK-MOH	MPK-MOH	MIBK-MOH	MAK-MOH
370	.0000	.0000	.0000	.0000	.0000	.7321	.7304	.7503
371	.0000	.0000	.0000	.0000	.0000	.7311	.7292	.7494
372	.0000	.0000	.0000	.0000	.0000	.7300	.7281	.7485
373	.0000	.0000	.0000	.0000	.0000	.7289	.7269	.7476
374	.0000	.0000	.0000	.0000	.0000	.7279	.7257	.7467
375	.0000	.0000	.0000	.0000	.0000	.7268	.7245	.7458
376	.0000	.0000	.0000	.0000	.0000	.0000	.7233	.7449
377	.0000	.0000	.0000	.0000	.0000	.0000	.7221	.7441
378	.0000	.0000	.0000	.0000	.0000	.0000	.7208	.7432
379	.0000	.0000	.0000	.0000	.0000	.0000	.7196	.7423
380	.0000	.0000	.0000	.0000	.0000	.0000	.7183	.7414

APPENDIX IV

VISCOSITY DATA FOR SYSTEMS STUDIED

TABLE 22. VISCOSITY DATA FOR SYSTEMS STUDIED (CENTIPOISES)

T	MOH-H2O	ATN-H2O	MEK-H2O	ATN-MOH	MEK-MOH	MPK-MOH	MIBK-MOH	MAK-MOH
190	5.8992	1.6613	2.9487	1.6246	2.8456	.0000	6.9712	.0000
191	5.7588	1.6291	2.8670	1.5913	2.7643	.0000	6.8745	.0000
192	5.6198	1.5973	2.7877	1.5586	2.6858	.0000	6.7629	.0000
193	5.4823	1.5660	2.7109	1.5266	2.6099	.0000	6.6391	.0000
194	5.3466	1.5352	2.6364	1.4953	2.5367	.0000	6.5047	.0000
195	5.2127	1.5050	2.5642	1.4647	2.4660	.0000	6.3618	.0000
196	5.0809	1.4752	2.4943	1.4348	2.3978	3.9090	6.2119	.0000
197	4.9513	1.4460	2.4266	1.4055	2.3319	3.8579	6.0565	.0000
198	4.8240	1.4173	2.3611	1.3769	2.2682	3.7998	5.8970	.0000
199	4.6991	1.3892	2.2976	1.3489	2.2068	3.7356	5.7348	.0000
200	4.5767	1.3616	2.2361	1.3216	2.1474	3.6665	5.5709	.0000
201	4.4568	1.3346	2.1765	1.2949	2.0900	3.5930	5.4063	.0000
202	4.3395	1.3081	2.1189	1.2688	2.0346	3.5163	5.2421	.0000
203	4.2249	1.2821	2.0632	1.2434	1.9811	3.4366	5.0789	.0000
204	4.1128	1.2567	2.0092	1.2185	1.9294	3.3552	4.9174	.0000
205	4.0034	1.2319	1.9569	1.1943	1.8795	3.2722	4.7582	.0000
206	3.8967	1.2075	1.9063	1.1706	1.8312	3.1884	4.6018	.0000
207	3.7927	1.1837	1.8574	1.1475	1.7846	3.1042	4.4485	.0000
208	3.6913	1.1605	1.8100	1.1250	1.7395	3.0201	4.2989	.0000
209	3.5926	1.1377	1.7641	1.1030	1.6959	2.9365	4.1530	.0000
210	3.4964	1.1155	1.7198	1.0815	1.6538	2.8535	4.0112	.0000
211	3.4029	1.0937	1.6768	1.0606	1.6130	2.7716	3.8734	.0000
212	3.3119	1.0725	1.6352	1.0402	1.5736	2.6910	3.7399	.0000
213	3.2234	1.0517	1.5950	1.0202	1.5355	2.6119	3.6107	.0000
214	3.1374	1.0315	1.5560	1.0008	1.4987	2.5344	3.4859	.0000
215	3.0538	1.0117	1.5183	.9819	1.4630	2.4588	3.3655	.0000
216	2.9726	.9924	1.4818	.9634	1.4286	2.3850	3.2494	.0000
217	2.8937	.9735	1.4464	.9453	1.3952	2.3132	3.1375	.0000
218	2.8172	.9551	1.4122	.9278	1.3629	2.2434	3.0299	.0000
219	2.7429	.9371	1.3790	.9106	1.3316	2.1756	2.9264	.0000

TABLE 22. VISCOSITY DATA CONTINUED

T	MOH-H2O	ATN-H2O	MEK-H2O	ATN-MOH	MEK-MOH	MPK-MOH	MIBK-MOH	MAK-MOH
220	2.6708	.9195	1.3469	.8939	1.3013	2.1100	2.8269	.0000
221	2.6008	.9024	1.3158	.8775	1.2720	2.0465	2.7314	.0000
222	2.5329	.8856	1.2857	.8616	1.2436	1.9850	2.6397	.0000
223	2.4670	.8693	1.2565	.8461	1.2161	1.9257	2.5517	.0000
224	2.4031	.8534	1.2282	.8310	1.1895	1.8684	2.4674	.0000
225	2.3412	.8378	1.2008	.8162	1.1637	1.8132	2.3865	.0000
226	2.2811	.8227	1.1743	.8018	1.1387	1.7599	2.3090	.0000
227	2.2228	.8079	1.1485	.7877	1.1144	1.7086	2.2347	.0000
228	2.1664	.7934	1.1236	.7740	1.0910	1.6592	2.1635	.0000
229	2.1116	.7793	1.0994	.7606	1.0682	1.6117	2.0954	.0000
230	2.0585	.7656	1.0760	.7476	1.0461	1.5659	2.0301	.0000
231	2.0071	.7521	1.0533	.7348	1.0247	1.5219	1.9675	.0000
232	1.9572	.7390	1.0312	.7224	1.0039	1.4796	1.9076	.0000
233	1.9088	.7263	1.0098	.7103	.9837	1.4389	1.8503	.0000
234	1.8620	.7138	.9891	.6984	.9642	1.3998	1.7953	.0000
235	1.8166	.7016	.9690	.6869	.9452	1.3623	1.7427	.0000
236	1.7725	.6897	.9495	.6756	.9268	1.3262	1.6923	.0000
237	1.7298	.6781	.9305	.6646	.9089	1.2915	1.6440	.0000
238	1.6884	.6668	.9121	.6539	.8915	1.2582	1.5977	.0000
239	1.6483	.6558	.8943	.6434	.8746	1.2262	1.5534	.0000
240	1.6094	.6450	.8770	.6332	.8583	1.1954	1.5109	.0000
241	1.5717	.6345	.8601	.6232	.8423	1.1658	1.4702	.0000
242	1.5352	.6242	.8438	.6134	.8269	1.1374	1.4311	.0000
243	1.4997	.6142	.8279	.6039	.8119	1.1101	1.3937	.0000
244	1.4654	.6044	.8125	.5946	.7973	1.0839	1.3577	.0000
245	1.4320	.5949	.7976	.5855	.7831	1.0587	1.3233	.0000
246	1.3997	.5855	.7830	.5766	.7693	1.0344	1.2902	2.1719
247	1.3684	.5764	.7689	.5679	.7558	1.0111	1.2585	2.0992
248	1.3380	.5675	.7551	.5595	.7428	.9887	1.2280	2.0310
249	1.3085	.5588	.7418	.5512	.7301	.9672	1.1987	1.9668

TABLE 22. VISCOSITY DATA CONTINUED

T	MOH-H2O	ATN-H2O	MEK-H2O	ATN-MOH	MEK-MOH	MPK-MOH	MIBK-MOH	MAK-MOH
250	1.2799	.5504	.7288	.5431	.7177	.9464	1.1706	1.9064
251	1.2521	.5421	.7162	.5352	.7057	.9265	1.1436	1.8494
252	1.2252	.5340	.7039	.5275	.6940	.9073	1.1177	1.7956
253	1.1991	.5261	.6920	.5199	.6826	.8888	1.0927	1.7448
254	1.1737	.5184	.6803	.5125	.6716	.8710	1.0687	1.6966
255	1.1491	.5108	.6690	.5053	.6608	.8538	1.0456	1.6510
256	1.1252	.5035	.6580	.4983	.6503	.8373	1.0234	1.6078
257	1.1020	.4963	.6473	.4914	.6400	.8214	1.0021	1.5667
258	1.0795	.4892	.6369	.4846	.6301	.8060	.9815	1.5276
259	1.0577	.4823	.6268	.4781	.6204	.7912	.9616	1.4904
260	1.0364	.4756	.6169	.4716	.6109	.7769	.9425	1.4550
261	1.0158	.4691	.6073	.4653	.6017	.7632	.9241	1.4211
262	.9958	.4626	.5979	.4591	.5927	.7499	.9064	1.3888
263	.9764	.4564	.5888	.4531	.5839	.7370	.8892	1.3580
264	.9575	.4502	.5799	.4472	.5754	.7246	.8727	1.3285
265	.9391	.4442	.5713	.4414	.5671	.7127	.8568	1.3002
266	.9213	.4384	.5628	.4358	.5590	.7011	.8414	1.2731
267	.9039	.4326	.5546	.4302	.5510	.6899	.8265	1.2471
268	.8871	.4270	.5466	.4248	.5433	.6791	.8121	1.2221
269	.8707	.4215	.5388	.4195	.5358	.6686	.7982	1.1981
270	.8548	.4162	.5312	.4144	.5284	.6585	.7848	1.1750
271	.8393	.4109	.5238	.4093	.5213	.6487	.7718	1.1527
272	.8242	.4058	.5166	.4043	.5142	.6392	.7592	1.1313
273	.8096	.4007	.5095	.3994	.5074	.6300	.7471	1.1107
274	.7954	.3958	.5026	.3947	.5007	.6210	.7353	1.0907
275	.7815	.3910	.4959	.3900	.4942	.6124	.7239	1.0715
276	.7680	.3863	.4893	.3854	.4879	.6040	.7129	1.0529
277	.7549	.3817	.4830	.3810	.4816	.5958	.7021	1.0349
278	.7422	.3772	.4767	.3766	.4756	.5879	.6918	1.0175
279	.7297	.3728	.4706	.3723	.4696	.5802	.6817	1.0006

TABLE 22. VISCOSITY DATA CONTINUED

T	MOH-H2O	ATN-H2O	MEK-H2O	ATN-MOH	MEK-MOH	MPK-MOH	MIBK-MOH	MAK-MOH
280	.7177	.3684	.4647	.3681	.4638	.5728	.6719	.9843
281	.7059	.3642	.4589	.3639	.4582	.5655	.6624	.9684
282	.6944	.3601	.4532	.3599	.4526	.5585	.6532	.9531
283	.6833	.3560	.4477	.3559	.4472	.5516	.6442	.9382
284	.6724	.3520	.4423	.3520	.4419	.5449	.6355	.9236
285	.6618	.3481	.4370	.3482	.4368	.5384	.6270	.9096
286	.6515	.3443	.4318	.3445	.4317	.5320	.6188	.8958
287	.6415	.3406	.4268	.3408	.4268	.5259	.6108	.8825
288	.6317	.3369	.4219	.3372	.4219	.5198	.6030	.8695
289	.6221	.3333	.4171	.3337	.4172	.5139	.5954	.8569
290	.6128	.3298	.4124	.3303	.4126	.5082	.5880	.8446
291	.6038	.3264	.4078	.3269	.4080	.5026	.5808	.8326
292	.5950	.3230	.4033	.3236	.4036	.4971	.5737	.8208
293	.5863	.3197	.3989	.3203	.3993	.4917	.5669	.8094
294	.5780	.3165	.3946	.3171	.3950	.4865	.5602	.7983
295	.5698	.3133	.3904	.3140	.3909	.4814	.5537	.7874
296	.5618	.3102	.3863	.3109	.3868	.4764	.5473	.7767
297	.5540	.3071	.3823	.3079	.3828	.4714	.5410	.7663
298	.5464	.3041	.3784	.3049	.3789	.4666	.5350	.7561
299	.5390	.3012	.3745	.3020	.3751	.4619	.5290	.7462
300	.5318	.2983	.3708	.2992	.3714	.4573	.5232	.7364
301	.5247	.2955	.3671	.2964	.3677	.4527	.5175	.7269
302	.5178	.2927	.3635	.2936	.3641	.4483	.5119	.7176
303	.5111	.2900	.3600	.2909	.3606	.4439	.5064	.7085
304	.5046	.2874	.3565	.2883	.3572	.4396	.5011	.6995
305	.4982	.2847	.3532	.2856	.3538	.4353	.4958	.6907
306	.4919	.2822	.3499	.2831	.3505	.4312	.4907	.6821
307	.4858	.2797	.3466	.2806	.3473	.4271	.4856	.6737
308	.4798	.2772	.3435	.2781	.3441	.4230	.4807	.6654
309	.4740	.2748	.3404	.2757	.3410	.4190	.4758	.6573

TABLE 22. VISCOSITY DATA CONTINUED

T	MOH-H2O	ATN-H2O	MEK-H2O	ATN-MOH	MEK-MOH	MPK-MOH	MIBK-MOH	MAK-MOH
310	.4683	.2724	.3374	.2733	.3379	.4151	.4710	.6494
311	.4628	.2701	.3344	.2710	.3350	.4113	.4663	.6416
312	.4573	.2678	.3315	.2687	.3320	.4075	.4617	.6339
313	.4520	.2655	.3286	.2664	.3291	.4037	.4572	.6264
314	.4469	.2633	.3258	.2642	.3263	.4000	.4527	.6190
315	.4418	.2612	.3231	.2620	.3236	.3963	.4483	.6118
316	.4369	.2590	.3204	.2599	.3209	.3927	.4440	.6047
317	.4320	.2569	.3178	.2578	.3182	.3891	.4398	.5977
318	.4273	.2549	.3152	.2557	.3156	.3856	.4356	.5908
319	.4227	.2529	.3127	.2537	.3130	.3821	.4315	.5840
320	.4182	.2509	.3103	.2517	.3105	.3786	.4274	.5774
321	.4137	.2490	.3078	.2497	.3080	.3752	.4234	.5709
322	.4094	.2470	.3055	.2478	.3056	.3718	.4194	.5644
323	.4052	.2452	.3031	.2459	.3033	.3684	.4156	.5581
324	.4011	.2433	.3009	.2440	.3009	.3651	.4117	.5519
325	.3970	.2415	.2986	.2422	.2986	.3618	.4079	.5458
326	.3931	.2398	.2964	.2404	.2964	.3585	.4042	.5398
327	.3892	.2380	.2943	.2386	.2942	.3553	.4004	.5339
328	.3854	.2363	.2922	.2368	.2920	.3521	.3968	.5281
329	.3817	.2346	.2901	.2351	.2899	.3489	.3932	.5224
330	.3781	.0000	.2881	.0000	.2878	.3457	.3896	.5167
331	.3745	.0000	.2861	.0000	.2858	.3426	.3861	.5112
332	.3711	.0000	.2842	.0000	.2837	.3394	.3826	.5058
333	.3677	.0000	.2823	.0000	.2818	.3363	.3791	.5004
334	.3643	.0000	.2804	.0000	.2798	.3333	.3757	.4951
335	.3611	.0000	.2785	.0000	.2779	.3302	.3723	.4899
336	.3579	.0000	.2767	.0000	.2761	.3272	.3689	.4848
337	.3548	.0000	.2750	.0000	.2742	.3241	.3656	.4798
338	.0000	.0000	.2732	.0000	.2724	.3211	.3623	.4748
339	.0000	.0000	.2715	.0000	.2706	.3181	.3590	.4699

TABLE 22. VISCOSITY DATA CONTINUED

T	MOH-H2O	ATN-H2O	MEK-H2O	ATN-MOH	MEK-MOH	MPK-MOH	MIBK-MOH	MAK-MOH
340	.0000	.0000	.2699	.0000	.2689	.3152	.3558	.4651
341	.0000	.0000	.2682	.0000	.2672	.3122	.3526	.4604
342	.0000	.0000	.2666	.0000	.2655	.3092	.3494	.4557
343	.0000	.0000	.2650	.0000	.2638	.3063	.3463	.4511
344	.0000	.0000	.2635	.0000	.2622	.3034	.3431	.4466
345	.0000	.0000	.2620	.0000	.2606	.3005	.3400	.4421
346	.0000	.0000	.2605	.0000	.2590	.2976	.3370	.4377
347	.0000	.0000	.2590	.0000	.2575	.2947	.3339	.4334
348	.0000	.0000	.2576	.0000	.2559	.2919	.3309	.4291
349	.0000	.0000	.2562	.0000	.2544	.2890	.3279	.4249
350	.0000	.0000	.2548	.0000	.2530	.2862	.3249	.4208
351	.0000	.0000	.2534	.0000	.2515	.2834	.3219	.4167
352	.0000	.0000	.2521	.0000	.2501	.2806	.3190	.4127
353	.0000	.0000	.0000	.0000	.0000	.2778	.3161	.4087
354	.0000	.0000	.0000	.0000	.0000	.2750	.3132	.4048
355	.0000	.0000	.0000	.0000	.0000	.2722	.3103	.4010
356	.0000	.0000	.0000	.0000	.0000	.2694	.3074	.3972
357	.0000	.0000	.0000	.0000	.0000	.2667	.3046	.3935
358	.0000	.0000	.0000	.0000	.0000	.2639	.3017	.3898
359	.0000	.0000	.0000	.0000	.0000	.2612	.2989	.3862
360	.0000	.0000	.0000	.0000	.0000	.2585	.2961	.3826
361	.0000	.0000	.0000	.0000	.0000	.2558	.2934	.3791
362	.0000	.0000	.0000	.0000	.0000	.2531	.2906	.3756
363	.0000	.0000	.0000	.0000	.0000	.2504	.2878	.3722
364	.0000	.0000	.0000	.0000	.0000	.2477	.2851	.3688
365	.0000	.0000	.0000	.0000	.0000	.2451	.2824	.3655
366	.0000	.0000	.0000	.0000	.0000	.2424	.2797	.3623
367	.0000	.0000	.0000	.0000	.0000	.2398	.2770	.3590
368	.0000	.0000	.0000	.0000	.0000	.2371	.2744	.3559
369	.0000	.0000	.0000	.0000	.0000	.2345	.2717	.3527

TABLE 22. VISCOSITY DATA CONTINUED

T	MOH-H2O	ATN-H2O	MEK-H2O	ATN-MOH	MEK-MOH	MPK-MOH	MIBK-MOH	MAK-MOH
370	.0000	.0000	.0000	.0000	.0000	.2319	.2691	.3497
371	.0000	.0000	.0000	.0000	.0000	.2293	.2665	.3466
372	.0000	.0000	.0000	.0000	.0000	.2268	.2639	.3436
373	.0000	.0000	.0000	.0000	.0000	.2242	.2613	.3407
374	.0000	.0000	.0000	.0000	.0000	.2216	.2587	.3378
375	.0000	.0000	.0000	.0000	.0000	.2191	.2562	.3349
376	.0000	.0000	.0000	.0000	.0000	.0000	.2536	.3321
377	.0000	.0000	.0000	.0000	.0000	.0000	.2511	.3293
378	.0000	.0000	.0000	.0000	.0000	.0000	.2486	.3265
379	.0000	.0000	.0000	.0000	.0000	.0000	.2461	.3238
380	.0000	.0000	.0000	.0000	.0000	.0000	.2436	.3212

APPENDIX V

VALUES OF THE GROUP $D\mu/T$ FOR VARIOUS SYSTEMS AS A FUNCTION OF TEMPERATURE

Table 23. Values of the Group $D\mu/T$ for Various Systems as a Function of Temperature

Part A - Self-diffusion Systems

Material	T° K.	$D \times 10^5$ cm^2/sec	$D\mu/T \times 10^{10}$	Ref.
Water	273	1.1	7.20	(2)
"	301	2.5	6.95	(2)
"	288	1.90	7.51	(2)
"	298	2.43	7.24	(2)
"	308	2.98	6.99	(2)
"	318	3.60	6.80	(2)
"	288	1.62	5.85	(2)
"	298	2.04	6.12	(2)
"	308	2.73	6.39	(2)
"	318	3.34	6.30	(2)
"	273	1.00	6.55	(2)
"	278	1.29	6.96	(2)
"	291	1.77	6.75	(2)
"	298	2.12	6.36	(2)
"	308	2.76	6.46	(2)
"	318	3.52	6.64	(2)
"	328	4.39	6.76	(2)
"	274	1.13	7.14	(2)
"	298	2.26	6.77	(2)
"	287	1.94	7.83	(2)
"	298	2.64	7.91	(2)
"	308	3.88	9.10	(2)
"	318	4.75	9.03	(2)
"	283	1.57	7.27	(2)
"	291	2.06	7.50	(2)
"	298	2.34	7.04	(2)
"	318	3.87	7.30	(2)
"	328	4.95	7.63	(2)
"	298	2.48	7.44	(38)
"	298	2.35	7.05	(38)
"	298	2.64	7.95	(2)

Table 23. Values of the Group $D\mu/T$ for Various Systems as a Function of Temperature (Part A - Continued)

Material	T° K.	$D \times 10^5$ cm^2/sec	$D\mu/T \times 10^{10}$	Ref.
Water	278	1.39	7.60	(2)
"	288	1.83	7.24	(2)
"	298	2.44	7.31	(2)
"	308	3.04	7.12	(2)
"	318	3.83	7.22	(2)
"	298	2.09	6.27	(2)
"	318	3.20	6.04	(2)
"	274	1.44	9.04	(2)
"	278	1.55	8.48	(2)
"	283	1.90	8.80	(2)
"	298	2.66	7.99	(2)
"	308	3.49	8.18	(2)
"	318	4.38	8.27	(2)
"	328	5.35	8.26	(2)
Benzene	288	1.88	4.56	(2)
"	298	2.15	4.36	(2)
"	308	2.40	4.13	(2)
"	318	2.67	3.98	(2)
"	298	2.18	4.42	(2)
n-Butanol	298	.504	4.36	(2)
"	308	.649	4.23	(2)
"	318	.822	4.09	(2)
t-Butanol	308	.497	2.83	(2)
"	318	.744	2.83	(2)
"	328	1.070	2.91	(2)
Ethanol	288	0.80	3.67	(2)
"	298	1.05	3.81	(2)
"	308	1.31	3.89	(2)
"	318	1.70	4.10	(2)
Ethanol	288	0.768	3.52	(2)
"	298	1.01	3.66	(2)
"	308	1.30	3.86	(2)
Ethanol	298	1.02	3.10	(2)

Table 23. Values of the Group $D\mu/T$ for Various Systems as a Function of Temperature (Part A - Continued)

Material	T° K.	$D \times 10^5$ cm^2/sec	$D\mu/T \times 10^{10}$	Ref.
Methanol	288	1.93	4.22	(2)
"	298	2.27	4.18	(2)
"	308	2.65	4.15	(2)
Methanol	298	2.36	4.34	(2)
Ethyl Bromide	288	3.60	5.23	(2)
"	296	3.80	4.93	(2)
"	303	3.96	4.69	(2)
i-Propanol	288	.474	4.15	(2)
"	298	.649	4.24	(2)
"	308	.867	4.40	(2)
"	318	1.145	4.30	(2)
n-Propanol	288	.504	4.40	(2)
"	298	.646	4.24	(2)
"	308	.814	4.08	(2)
"	318	1.017	4.00	(2)
Carbon tetrachloride	298	1.41	4.25	(2)
"	308	1.75	4.47	(2)
"	318	1.99	4.35	(2)
Carbon tetrachloride	298	1.30	3.93	(37)
"	313	1.78	4.18	(37)
"	323	2.00	4.04	(37)
"	333	2.44	4.27	(37)
Benzene	280	1.42	4.04	(37)
"	288	1.70	4.14	(37)
"	298	2.21	4.49	(37)
"	308	2.51	4.33	(37)
"	318	2.81	4.16	(37)
"	328	3.56	4.57	(37)
"	338	4.07	4.57	(37)
Ethanol	280	.618	3.42	(37)
"	288	.810	3.72	(37)
"	298	1.02	3.70	(37)
"	308	1.28	3.80	(37)
"	318	1.65	3.87	(37)
"	328	2.06	4.08	(37)
"	338	2.61	4.24	(37)

Table 23. Values of the Group $D\mu/T$ for Various Systems as a Function of Temperature (Part A - Concluded)

Material	T° K.	D × 10^5 cm^2/sec	$D\mu/T \times 10^{10}$	Ref.
Methanol	268	1.26	4.04	(37)
"	278	1.55	4.17	(37)
"	288	1.91	4.18	(37)
"	298	2.34	4.30	(37)
"	308	2.74	4.27	(37)
"	313	2.89	4.16	(37)
"	318	3.37	4.45	(37)
"	328	3.88	4.37	(37)
n-Pentane	298	5.62	4.08	(19)
n-Hexane	298	4.21	4.15	(19)
n-Heptane	298	3.12	4.04	(19)
"	273	2.08	4.00	(19)
n-Octane	298	2.00	3.42	(19)
n-Nonane	298	1.70	3.77	(19)
n-Decane	298	1.31	3.75	(19)
n-Octadecane	323	0.46	3.33	(19)
n-$C_{32}H_{66}$	373	0.30	4.31	(19)
2-Methyl butane	298	5.30	3.90	(19)
2,2-Dimethyl propane	298	4.86	3.72	(19)
2-Methyl pentane	298	3.98	3.94	(19)
3-Methyl pentane	298	3.61	3.73	(19)
2,2-Dimethyl butane	298	3.41	4.02	(19)
2,3-Dimethyl butane	298	3.50	4.24	(19)
Nitromethane	298	2.11	4.40	(19)
Acetone	298	4.77	4.91	(19)
Cyclohexane	298	1.38	4.18	(19)

Table 23. Values of the Group $D\mu/T$ for Various Systems as a Function of Temperature

Part B - Binary Diffusion Systems

Solute	Solvent	T° K.	$D \times 10^5$ cm^2/sec	$D\mu/T \times 10^{10}$	Ref.
$N\text{-}C_5H_{12}$	Carbon tetrachloride	323	3.05	6.07	(39)
$N\text{-}C_{10}H_{22}$	"	323	1.90	3.84	(39)
$N\text{-}C_{18}H_{38}$	"	323	1.16	2.22	(39)
$N\text{-}C_{28}H_{58}$	"	323	0.75	1.51	(39)
$N\text{-}C_{35}H_{72}$	"	323	0.70	1.40	(39)
Benzoic Acid	Carbon tetrachloride	288	0.78	2.82	(40)
"	"	298	0.91	2.76	(40)
"	"	314	1.17	2.74	(40)
"	Benzene	288	1.17	2.83	(40)
"	"	298	1.38	2.79	(40)
"	"	313	1.76	2.78	(40)
"	Toluene	289	1.29	2.76	(40)
"	"	298	1.49	2.77	(40)
"	"	313	1.85	2.78	(40)
"	Acetone	286	2.37	2.82	(40)
"	"	298	2.62	2.75	(40)
"	"	313	3.05	2.73	(40)
"	Ethylene Glycol	298	0.043	2.49	(40)
"	"	323	0.18	3.77	(40)
Acetic Acid	Carbon tetrachloride	280	1.15	4.94	(40)
"	"	288	1.27	4.63	(40)
"	"	298	1.49	4.53	(40)
"	"	313	1.78	4.15	(40)
"	Benzene	279	1.58	4.62	(40)
"	"	298	2.09	4.22	(40)
"	Toluene	280	1.66	4.16	(40)
"	"	288	1.90	4.10	(40)
"	"	298	2.26	4.19	(40)

Table 23. Values of the Group $D\mu/T$ for Various Systems as a Function of Temperature (Part B - Continued)

Solute	Solvent	T° K.	$D \times 10^5$ cm^2/sec	$D\mu/T \times 10^{10}$	Ref.
Acetic Acid	Acetone	288	2.92	3.41	(40)
"	"	298	3.31	3.46	(40)
"	"	313	4.40	3.45	(40)
"	Ethylene glycol	288	0.039	3.5	(40)
"	"	298	0.13	7.4	(40)
"	"	303	0.20	8.8	(40)
Cinnamic Acid	Carbon tetra-chloride	298	0.76	2.30	(40)
"	Benzene	298	1.12	2.25	(40)
"	Toluene	298	1.18	2.18	(40)
"	Acetone	298	2.41	2.52	(40)
Formic Acid	Carbon tetra-chloride	282	1.61	6.65	(40)
"	"	288	1.67	6.08	(40)
"	"	298	1.89	5.74	(40)
"	Benzene	279	1.99	5.81	(40)
"	"	287	2.31	5.72	(40)
"	"	298	2.28	5.21	(40)
"	Toluene	279	2.28	5.77	(40)
"	"	287	2.46	5.44	(40)
"	"	298	2.65	4.90	(40)
"	Acetone	280	3.13	4.14	(40)
"	"	287	3.27	3.95	(40)
"	"	298	3.77	3.94	(40)
"	Ethylene glycol	298	0.094	5.5	(40)
"	"	323	0.220	4.4	(40)
Iodine	$CH_3(CH_2)_{12}CH_3$	298	0.96	6.81	(40)
"	n-Octane	288	2.43	4.89	(40)
"	"	298	2.76	4.71	(40)
"	"	313	3.22	4.29	(40)
"	n-Hexane	298	4.24	4.31	(40)
"	Cyclo-hexane	288	1.54	5.65	(40)
"	"	303	1.92	5.21	(40)
"	"	313	2.30	5.17	(40)

Table 23. Values of the Group $D\mu/T$ for Various Systems as a Function of Temperature (Part B - Continued)

Solute	Solvent	T° K.	$D \times 10^5$ $cm.^2/sec$	$D\mu/T \times 10^{10}$	Ref.
Iodine	Methyl cyclohexane	303	2.30	4.74	(40)
"	"	313	2.71	4.86	(40)
"	Ethanol	298	1.32	4.71	(40)
"	"	313	1.77	4.65	(40)
"	C_6H_5Br	303	1.39	4.53	(40)
"	Carbon tetrachloride	303	1.61	4.57	(40)
Carbon Dioxide	Water	280	1.145	5.93	(41)
"	"	298	1.85	5.55	(41)
"	"	308	2.18	5.11	(41)
"	"	325	3.61	5.90	(41)
"	"	338	4.30	5.55	(41)
Sucrose	Water	298	0.524	1.57	(42)
"	"	323	0.93	1.57	(42)
"	"	343	1.36	1.62	(42)
Methanol	Water	287.5	1.23	4.93	(43)
"	"	294	1.40	4.68	(43)
"	"	303	1.70	4.49	(43)
"	"	313	2.10	4.40	(43)
"	"	323	2.55	4.37	(43)
Acetamide	Water	285.5	0.84	3.59	(43)
"	"	294	1.06	3.55	(43)
"	"	303	1.33	3.51	(43)
"	"	313	1.60	3.34	(43)
"	"	323	1.80	3.06	(43)
Glycerin	Water	285.5	0.57	2.44	(43)
"	"	294	0.72	2.41	(43)
"	"	303	0.92	2.43	(43)
"	"	313	1.09	2.28	(43)
"	"	323	1.26	2.15	(43)
Sucrose	Water	285.5	0.40	1.71	(43)
"	"	294	0.45	1.51	(43)
"	"	303	0.56	1.48	(43)
"	"	313	0.69	1.44	(43)
"	"	323	0.84	1.43	(43)
"	"	333	1.03	1.47	(43)

Table 23. Values of the Group $D\mu/T$ for Various Systems as a Function of Temperature (Part B - Continued)

Solute	Solvent	T° K.	$D \times 10^5$ cm^2/sec	$D\mu/T \times 10^{10}$	Ref.
m-Digallic Acid	Water	285.5	0.22	0.94	(43)
"	"	294	0.24	0.805	(43)
"	"	303	0.30	0.792	(43)
"	"	313	0.37	0.774	(43)
"	"	323	0.45	0.765	(43)
Dextron	Water	294	0.042	0.141	(43)
"	"	303	0.050	0.132	(43)
"	"	313	0.062	0.129	(43)
"	"	323	0.074	0.126	(43)
"	"	333	0.088	0.125	(43)
Polyvinyl Alcohol	Water	294	0.029	0.970	(43)
"	"	303	0.033	0.870	(43)
"	"	313	0.041	0.857	(43)
"	"	323	0.050	0.850	(43)
"	"	327.5	0.054	0.850	(43)
Methanol	Acetone	195	0.521	3.91	This work
"	"	233	1.45	4.41	"
"	"	253	1.86	3.82	"
"	"	273	2.83	4.15	"
"	"	293	3.72	4.07	"
"	"	323	5.10	3.89	"
Methanol	MEK	195	0.409	4.50	"
"	"	233	1.00	4.21	"
"	"	253	1.52	4.10	"
"	"	273	2.57	4.78	"
"	"	293	3.20	4.35	"
"	"	323	5.32	4.98	"
Methanol	MPK	195	0.227	4.60	"
"	"	233	0.781	4.80	"
"	"	253	1.38	4.85	"
"	"	273	2.01	4.63	"
"	"	293	2.53	4.25	"
"	"	323	4.02	4.58	"
"	"	353	6.80	5.35	"

Table 23. Values of the Group Dμ/T for Various Systems as a Function of Temperature (Part B - Concluded)

Solute	Solvent	T° K.	D × 10^5 cm^2/sec	Dμ/T × 10^{10}	Ref.
Methanol	MiBK	195	0.126	4.11	This work
"	"	233	0.559	4.42	"
"	"	253	0.930	4.02	"
"	"	273	1.38	3.78	"
"	"	293	1.97	3.82	"
"	"	323	3.09	3.98	"
"	"	353	4.09	3.66	"
"	"	368	5.40	4.02	"
Methanol	MnAK	253	0.819	5.65	"
"	"	273	1.15	4.68	"
"	"	293	1.93	5.32	"
"	"	323	3.38	5.73	"
"	"	368	6.18	5.96	"
Water	Water	298	2.35	7.05	"
Methanol	Water	288	1.33	5.27	"
Water	Methanol	195	0.137	3.66	"
"	"	233	0.495	4.06	"
"	"	253	0.829	3.89	"
"	"	273	1.37	4.05	"
"	"	293	1.79	3.59	"
"	"	323	2.73	3.42	"
Water	Acetone	195	0.62	4.79	"
"	"	233	1.34	4.18	"
"	"	253	2.15	4.48	"
"	"	273	2.98	4.45	"
"	"	293	3.87	4.23	"
"	"	323	5.58	4.23	"
Water	MEK	195	0.260	3.43	"
"	"	233	0.977	4.21	"
"	"	253	1.47	4.02	"
"	"	273	2.15	4.01	"
"	"	293	2.89	3.94	"
"	"	323	4.16	3.91	"

APPENDIX VI

SAMPLE CALCULATION OF THE DIFFUSION COEFFICIENT

APPENDIX VI

SAMPLE CALCULATION OF THE DIFFUSION COEFFICIENT

The mathematical model for the tracer concentration of the stirred bath developed in Chapter II stated that if the logarithm of

$$(1 - C_{Bt}/C_{B\infty}) \tag{5.1}$$

is plotted versus time, a straight line of slope $-DK_F$ should result. Table 24 shows the data taken from runs M 25 and M 26 in order to determine the diffusion coefficient of water in methanol at 293° K. Figure 22 presents the same data in graphical form.

In order to determine the slope, a graph of the data was prepared for each run as a check for any data points which were obviously erroneous. The time and $(1 - C_{Bt}/C_{B\infty})$ data points were then used as input for a computer program which computed the slope between all data points not adjacent and which found the best value for the slope by a least squares curve fitting method.

Table 25 shows the computed data for runs M 25 and M 26. As the difference between the values for the slopes was less than 10 percent, the criteria for acceptance was met and the slope was determined to be -4.88×10^{-2}/minute.

This slope was divided by the frit calibration constant, 2.68×10^{3}, and diffusion coefficient of 1.82×10^{-5} cm^2/sec was determined for tritiated water in methanol at 293° K.

Table 24. Data from Runs M 25 and M 26

Run #	Time (min)	C_t (cpm)	C_t/C_∞	$(1 - C_t/C_\infty)$
M 25	3.25	24701	0.4705	0.5295
	4.0	27748	0.5276	0.4724
	6.0	33204	0.6324	0.3676
	7.0	35051	0.6667	0.3333
	10.0	39083	0.7447	0.2553
	11.0	42124	0.8019	0.1981
	14.0	44929	0.8553	0.1447
	15.0	44491	0.8476	0.1524
	17.0	45983	0.8758	0.1242
	∞	51480		
	∞	52786		
	∞	52690		
M 26	4.0	29578	0.4958	0.5042
	5.0	35269	0.5932	0.4068
	7.0	40002	0.6732	0.3277
	10.0	46437	0.7798	0.2207
	11.0	47521	0.7983	0.2017
	13.0	49092	0.8252	0.1748
	14.0	49893	0.8385	0.1615
	16.0	52163	0.8766	0.1234
	17.0	53771	0.9037	0.0963
	∞	59394		
	∞	59844		
	∞	59290		

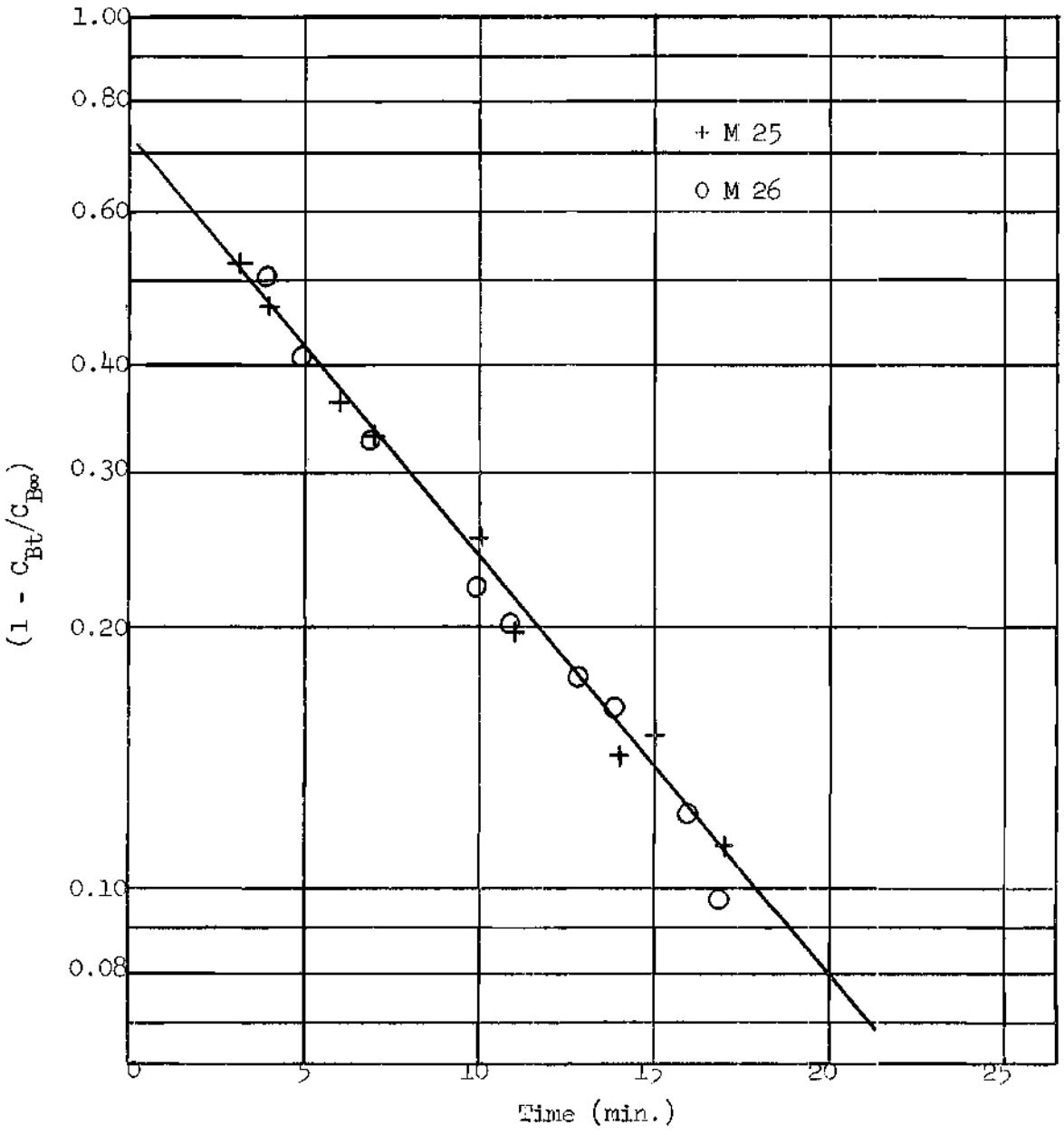

Figure 22. Graph of Data from Runs M 25 and M 26 for Diffusion of H_2C in MeOH at 293° K.

Table 25. Computed Slopes for Runs M 25 and M 26

Run M 25

t_1 (min)	$\text{Log}(1 - C_{t1}/C_\infty)$	t_2 (min)	$\text{Log}(1 - C_{t2}/C_\infty)$	- Slope × 10^2
3.25	-.27608	6.00	-.43454	5.76
		7.00	-.47707	5.36
		10.00	-.59284	4.69
		11.00	-.70298	5.51
		14.00	-.83938	5.24
		15.00	-.81686	4.60
		17.00	-.90571	4.58
4.00	-.32563	7.00	-.47707	5.05
		10.00	-.59284	4.45
		11.00	-.70298	5.39
		14.00	-.83938	5.14
		15.00	-.81686	4.47
		17.00	-.90571	4.46
6.00	-.43454	10.00	-.59284	3.96
		11.00	-.70298	5.37
		14.00	-.83938	5.06
		15.00	-.81686	4.25
		17.00	-.90571	4.28
7.00	-.47707	11.00	-.70298	5.65
		14.00	-.83938	5.18
		15.00	-.81686	4.25
		17.00	-.90571	4.29
10.00	-.59284	14.00	-.83938	6.16

Table 25. Computed Slopes for Runs M 25 and M 26
(Concluded.)

Run M 26

t_1 (min)	$\text{Log}(1 - C_{t1}/C_\infty$	t_2(min)	$\text{Log}(1 - C_{t2}/C_\infty)$	- Slope × 10^2
4.00	-.29734	7.00	-.48443	6.24
		10.00	-.65706	6.00
		11.00	-.65916	5.68
		13.00	-.75732	5.11
		14.00	-.79168	4.94
		16.00	-.90852	5.09
		17.00	-1.01619	5.52
5.00	-.39054	10.00	-.65706	5.33
		11.00	-.69516	5.08
		13.00	-.75732	4.58
		14.00	-.79168	4.45
		16.00	-.90852	4.71
		17.00	-1.01619	5.21
7.00	-.48443	11.00	-.69516	5.27
		13.00	-.75732	4.55
		14.00	-.79168	4.39
		16.00	-.90852	4.71
		17.00	-1.01619	5.32
10.00	-.65706	13.00	-.75732	3.34
		14.00	-.79168	3.36
		16.00	-.90852	4.19
		17.00	-1.01619	5.13
11.00	-.69516	14.00	-.79168	3.21

Run #	Slope × 10^2	Sum of Squares × 10^3	Population Variance × 10^5
M 25	4.92	.754	3.42
	4.96	.759	
	4.86	.760	
M 26	4.84	1.356	6.15
	4.89	1.361	
	4.79	1.361	

APPENDIX VII

COMPARISON OF VALUES FOR $\frac{D\mu}{T}$ CALCULATED FROM EQUATION 6.8 WITH EXPERIMENTAL VALUES

Table 26. Comparison of Values for $\frac{D\mu}{T}$ Calculated from Equation 6.8 with Experimental Values

Solute	Solvent	$D\mu/T \times 10^{10}$ Calc.	$D\mu/T \times 10^{10}$ Exp.	Δ %	Ref.
Carbon Dioxide	Water	5.76	6.21	+ 4	(43)
Methanol	"	5.12	4.58	+ 12	(43)
Acetamide	"	3.99	3.40	+ 17	(43)
Glycerol	"	3.25	2.40	+ 35	(43)
Sucrose	"	1.70	1.48	+ 15	(43)
Sucrose	"	1.70	1.57	+ 8	(42)
Raffinose	"	1.27	1.24	+ 2	(1)
Acetonitrite	Methanol	5.88	4.43	- 24	(1)
Chloroacetic Acid	"	3.54	3.39	+ 5	(1)
Urethane	"	3.23	2.87	+ 12	(1)
Carbon Tetrachloride	"	3.20	3.78	- 15	(1)
Iodoform	"	2.80	2.96	- 5	(1)
2,4,6-Trichloro-phenol	"	2.45	2.69	- 9	(1)
Dibenzyl Amine	"	1.98	1.92	+ 3	(1)
Formic Acid	Benzene	4.61	5.60	- 17	(40)
Acetic Acid	"	3.64	4.42	- 17	(40)
Benzoic Acid	"	2.63	2.79	- 5	(40)
Cinnamic Acid	"	2.14	2.25	- 4	(40)
Water	Acetone	6.90	4.40	+ 56	
Formic Acid	"	4.35	3.95	+ 10	(40)
Methanol	"	4.33	4.00	+ 8	
Acetic Acid	"	3.44	3.43	0	(40)

Table 26. Comparison of Values for $\frac{D\mu}{T}$ Calculated from Equation 6.8 with Experimental Values (Concluded)

Solute	Solvent	$D\mu/T \times 10^{10}$ Calc.	$D\mu/T \times 10^{10}$ Exp.	Δ %	Ref.
Bromoform	Acetone	2.70	3.00	- 10	(1)
Benzoic Acid	"	2.48	2.76	- 9	(40)
Formic Acid	Carbon tetrachloride	5.91	6.10	- 3	(40)
Acetic Acid	"	4.68	4.55	+ 2	(40)
Iodine	"	4.40	4.57	- 2	(40)
Benzene	"	3.74	4.27	- 12	(2)
Benzoic Acid	"	3.40	2.78	+ 22	(40)
Cinnamic Acid	"	2.75	2.30	+ 17	(40)
Bromoform	Ethanol	3.85	4.80	- 19	(16)
Iodine	"	4.62	4.80	- 4	(1)
i-Amyl Alcohol	"	3.39	3.19	+ 6	(16)
Phenol	"	3.77	3.28	+ 15	(1)
Formic Acid	Toluene	5.41	5.40	0	(40)
Acetic Acid	"	4.28	4.13	+ 4	(40)
Benzoic Acid	"	3.09	2.77	+ 11	(40)
Cinnamic Acid	"	2.52	2.18	+ 16	(40)

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Wilke, C. R., Chemical Engineering Progress, 45, 218 (1949)

2. Johnson, P. A., and A. L. Babb, Chemical Reviews, 56, 387 (1956)

3. Wall, F. T., P. F. Grieger, and C. W. Childers, Journal of the American Chemical Society, 74, 3562 (1952)

4. Nelson, F., and K. A. Kraus, Production and Use of Short Lived Isotopes from Reactors, Vol. I, International Atomic Energy Association, Vienna, (1962), 191

5. Einstein, A., Annalen der Physik, 17, 549 (1905)

6. Page, L., Introduction to Theoretical Physics, Van Nostrand Co., Inc., New York, (1935), 268

7. Powell, R. E., W. E. Roseveare, and H. Eyring, Industrial and Engineering Chemistry, 33, 430 (1941)

8. Graupner, K., and E. R. S. Winter, Journal of the Chemical Society, 1952, 1145 (1952)

9. Eyring, H., and T. Ree, Proceedings of the National Academy of Sciences of the United States of America, 47, 526 (1961)

10. Eyring H., and R. P. Marchi, Journal of Chemical Education, 40, 562 (1963)

11. Arnold, J. H., Journal of the American Chemical Society, 52, 3937 (1930)

12. Caldwell, C. S., and A. L. Babb, Journal of Physical Chemistry, 60, 51 (1956)

13. Kamal, M. R. and L. N. Canjar, American Institute of Chemical Engineers Journal, 8, 329 (1962)

14. Li, J. C. M. and P. Chang, Journal of Chemical Physics, 23, 518 (1955)

15. Reid, C. R. and T. R. Sherwood, The Properties of Gases and Liquids, McGraw-Hill Book Co., Inc., New York (1958), 51

16. Wilke, C. R. and Pin Chang, A. J. Ch. E. Journal, 1, 264 (1955)

BIBLIOGRAPHY (Continued)

17. Othmer, D. F., and M. S. Thakar, Ind. and Eng. Chem., 45, 589 (1953)

18. Scheibel, E. G., Ind. and Eng. Chem., 46, 2007 (1954)

19. Houghton, G., J. Chem. Phys., 40, 1628 (1964)

20. Carslaw, H. S. and J. C. Jaeger, Conduction of Heat in Solids, Oxford University Press, London, (1959), 97

21. Edwards, J. B., Vapor-Liquid Equilibria in Nitroparaffin-Hydrocarbon Systems which Exhibit Partial Miscibility, Unpublished Ph.D. Thesis, Georgia Institute of Technology (1963), 49

22. Hodgman, C. D., ed., Handbook of Chemistry and Physics, 38th Edition, Chemical Rubber Publishing Co., Cleveland (1956), 2063

23. Ibid., 2065

24. Union Carbide Technical Information Folder #F-40249, Union Carbide Chemical Company, Union Carbide Chemical Corp., New York, (March, 1959)

25. Hayes, F. N., Packard Technical Bulletin #1, Packard Instrument Company, Inc., La Grange, Illinois, (April, 1963)

26. Gianque, W. F., and C. J. Egan, J. Chem. Phys., 5, 45 (1937)

27. Zwolinski, B. J., ed., Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, American Petroleum Institute Research Project 44, Agricultural and Mechanical College of Texas, College Station, Texas, (1963)

28. Lange, N. A., ed., Handbook of Chemistry, 10th Ed., McGraw-Hill Book Co., Inc., New York, (1961), 1479

29. Hodgman, C. D., Op. cit., 1990

30. Ibid., 2030

31. Kimura, O., Journal of the Chemical Society of Japan, 63, 426 (1942)

32. Lange, N. A., Op. cit., 1657

33. Johnson, P. A. and A. L. Babb, Chem. Rev., 56, 387 (1956)

34. Mickley, H. S., T. K. Aherwood, and C. E. Reed, Applied Mathematics in Chemical Engineering, McGraw-Hill Book Co., Inc., New York, (1957), 68

BIBLIOGRAPHY (Concluded)

35. Ibid., 57

36. Ibid., 64

37. Rathbun, R. E., and A. L. Babb, J. Phys. Chem., 65, 1072 (1961)

38. Douglas, D. C., and D. W. McCall, J. Chem. Phys., 37, 569 (1961)

39. McCall, D. W. and D. C. Douglas, J. Chem. Phys., 38, 2314 (1962)

40. Chang, P. and C. R. Wilke, J. Phys. Chem., 59, 592 (1955)

41. Unver, A. A., and D. M. Himmelblau, Journal of Chemical Engineering Data, 9, 428 (1964)

42. Henrion, P. N., Transactions of the Faraday Society, 60, 72 (1964)

43. Mareenen, V. A., Vestnik Lenningradskogo Universiteta, 16, 44 (1957)

VITA

David Bowen, Jr. was born in Cairo, Georgia, on March 10, 1936. He graduated from Cairo High School, Cairo, Georgia, in June of 1954.

He entered the Georgia Institute of Technology in September of 1954 and was awarded the degree of Bachelor of Chemical Engineering in June of 1958.

Immediately after graduating, he completed the R.O.T.C. summer training program, was commissioned as a Second Lieutenant in the Regular Army, and ordered to active duty. During his tour of duty with the army, he completed courses of instruction at the Air Defense Artillery Center, Ft. Bliss, Texas, and the Army Demolition Training School, Murnau, Germany. He was released from active duty in October of 1961.

He entered the Graduate Division of the Georgia Institute of Technology in January of 1962 and completed the requirements for the degree Master of Science in Chemical Engineering in March of 1963.

He was awarded the Kaiser Chemical Company Fellowship for the academic years 1961-1962 and 1962-1963.

In 1956 he married the former Dorothy Luvoise Collins of Cairo, Georgia. They have three children, David III, Phillip Wesley, and Richard Russell.